PROCEEDINGS

OF THE

ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND PHYSICAL CHARACTER.

VOL. CIV.

LONDON:

PRINTED FOR THE ROYAL SOCIETY AND SOLD BY
HARRISON AND SONS, LTD., ST. MARTIN'S LANE,
PRINTERS IN ORDINARY TO HIS MAJESTY.

DECEMBER, 1923.

LONDON:

HARRISON AND SONS, LTD., PRINTERS IN ORDINARY TO HIS MAJESTY,

ST. MARTIN'S LANE.

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OBITUARY NOTICES OF FELLOWS DECEASED.

PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

Investigations on X-Rays and β-Rays by the Cloud Method. Part 1.—X-Rays.

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(Received June 23, 1923.)

(From the Solar Physics Observatory, Cambridge.)

[Plates 1–12.]

1. *Introduction.*

The method used in these investigations is that which was described in papers communicated to the Royal Society in 1911 and 1912.* The ionising rays are made to pass through moist air, or other gas, in which the water-vapour has been brought into the super-saturated state by sudden expansion of the gas. Each ion liberated becomes at once the nucleus for the condensation of a visible droplet of water; the clouds of drops thus formed are immediately photographed.

Very sharply defined pictures of the tracks of ionising particles—α- or β-rays—may be obtained in this way. When the conditions are suitably arranged, the effects of diffusion of the ions before their mobility has been destroyed by condensation of water upon them, as well as that of subsequent disturbance of the cloud tracks by convection currents in the gas, are negligible: photographs of the path of the ionising particles, practically free from distortion, are obtained. The almost perfect straightness of the track of a very fast β-particle, when it occurs among a crowd of tracks of slower β-particles, gives very convincing evidence that the complicated forms of the latter are not due to instrumental distortion.

* 'Roy. Soc. Proc.,' A, vol. 85, p. 285, and vol. 87, p. 277.

The information contained in the pictures is greatly increased when two cameras are used to take simultaneous photographs. For the purposes of exact measurement relating to some definite problem, such as the branching of α-ray tracks, the arrangement used by Shimizu* and others, in which the axes of the cameras are at right angles, has undoubted advantages. But for the purpose of disentangling the complicated phenomena which attend the passage of β-rays and X-rays through air the stereoscopic method is more effective; it has been used throughout the present investigations.

For the quantitative study of X-rays the cloud method has many advantages over that in which an ordinary ionisation chamber and electrometer are used. It gives directly the number and nature of the β-particles ejected from atoms by the X-rays, and not merely the total ionisation; if each β-ray which is produced by the action of the X-rays represents the absorption of one quantum of radiation the method enables us to deal directly with individual quanta. When the cloud châmber is momentarily traversed by a beam of X-radiation of suitable intensity a picture is obtained (in three dimensions if the stereoscopic method is used) of the tracks of all the electrons ejected from the atoms in a given volume of the gas by the action of the X-rays, primary and secondary. An inspection of the picture shows at once (1) the point of origin of each β-ray, (2) its initial direction (*i.e.*, the direction in which an electron has been ejected from its parent atom by the action of the radiation), (3) the total length of its path or range, (4) the form of the track, its sudden or gradual bends, and the number and direction of emission of any secondary β-rays (branches), and (5) the variation of the ionisation along the track; under favourable conditions the number and distribution of the ions along the tracks may be obtained by direct counting.

A number of stereoscopic pictures of the tracks of α- and β-particles with others illustrating the effects of X-rays, were taken early in 1914, but the work was then interrupted by the War. Some of these pictures were exhibited on different occasions at the Royal Society and elsewhere. Considerable improvements in the details of the method have been introduced since that time. Most of the photographs now reproduced belong to a series of nearly 500 stereoscopic pairs which were taken between December, 1921, and the end of July, 1922.

* 'Roy. Soc. Proc.,' A, vol. 99, p. 432 (1921).

2. *Improvements in the apparatus and method.*

The expansion apparatus which has been used throughout these investigations is that described and figured in the 1912 paper. The following are some of the improvements which have been made in the details of the method.

Cloud-chamber.—In most of the experiments the cloud-chamber consisted of a thin-walled glass cylinder 1·2 mm. thick, 16·5 cm. in diameter, with a plate-glass roof. The height from the top of the brass plunger, which formed the floor, to the roof of the cloud-chamber was generally 3 cm. As in the previous experiments, a marginal ring of tinfoil cemented in between the roof and walls of the cloud-chamber made it possible to maintain a potential difference between the roof and floor. The inner surfaces of the roof and sides of the cloud-chamber were at first coated as in the earlier experiments with a thin layer of gelatine; a small quantity of copper sulphate was added to the gelatine to prevent the growth of mould.

The gelatine lining does not remain permanently effective in preventing the formation of droplets on the interior of the roof and walls of the cloud-chamber. If the upper part of the apparatus remains for some time at a lower temperature than the base, as frequently happens at night owing to changes in room temperature, water distils rapidly from the floor to the roof and sides of the cloud-chamber and collects in drops which are not readily removed. To avoid this difficulty completely it is only necessary to keep the base of the cloud-chamber at a slightly lower temperature than the roof and sides. This is most effectively done by keeping the brass expansion cylinder at a temperature slightly below that of the room by allowing a small flow of tap water to pass continuously through the shallow receptacle in which the expansion cylinder rests.

When the base of the expansion apparatus is cooled in this way the walls and roof remain perfectly clear for an indefinite time, even when the gelatine lining is omitted altogether. Most of the recent photographs have been taken without any gelatine lining on the roof and sides of the cloud-chamber.

The floor of the cloud-chamber, formed by the upper surface of the plunger, remains as in the earlier work covered with a thick layer of gelatine; this is blackened by ink and contains a small quantity of copper sulphate in solution. As in the earlier experiments, a vertical electric field was maintained in the cloud-chamber; the field was directed upwards, and in most cases amounted to about 3 volts per cm.

Cameras.—Two simple box-cameras of fixed focus have been used to obtain the stereoscopic pictures; they are joined rigidly together with the centres

of their lenses 5·5 cm. apart. The lenses were Beck "Isostigmars" of maximum aperture F 5·8 and focal length 12 cm.; in many cases the aperture was reduced to F 8 or F 11. The axes of the two cameras converged to a point 40 cm. in front of the lenses for which distance they are also focussed. They have generally been used with their axes in the horizontal plane which passes through the centre of the cloud-chamber.

Illumination.—A Leyden jar discharge through mercury vapour at atmospheric pressure was used as before to illuminate the clouds for the purpose of obtaining the photographs. The mercury discharge tube was as shown in fig. 2 of the 1912 paper, but pointed steel rods were used to close the ends of the silica tubes; the ends of the tubes were inserted in mercury cups. The discharge tube was placed as before at the principal focus of a cylindrical lens.

Photographic plates.—"Imperial process" plates have been used in all the recent work. They are not appreciably less sensitive than rapid plates for the light from the mercury spark, and they have the great advantages of fineness of grain and convenience in use.

Timing Arrangements.—In order that sharply defined pictures may be obtained of the tracks of electrons ejected from atoms byX-rays, it is necessary that the rays should traverse the cloud chamber immediately after the sudden expansion of the gas, and that the drops which condense on the ions set free along the tracks should be momentarily illuminated after a very short interval. As in the early experiments, the momentary flash of X-radiation which sets free the ions in the cloud chamber and the mercury vapour spark which illuminates the drops condensed upon them are produced by the discharge of Leyden jars. The old arrangement in which a falling sphere brought about the two discharges in succession, has been replaced by one in which three pendulums of adjustable period are all released simultaneously. The first (the "expansion" pendulum), as it reaches the lowest point of its swing, opens communication between the vacuum chamber and the space below the plunger, the others (the "X-ray" pendulum and "spark" pendulum) as they reach their lowest points discharge Leyden jars through the X-ray bulb and mercury discharge tube respectively. By adjustment of sliding weights on these pendulums, the X-rays may be made to traverse the expansion apparatus immediately after the expansion is completed, while the illuminating spark follows at an interval long enough to enable the cloud particles to condense on the ions, but not long enough to allow of convection currents causing distortion of the tracks.

When the rays from radio-active substances are being studied, a somewhat

larger potential difference (from 20 to 100 volts) has generally been maintained between the roof and floor of the cloud-chamber than in experiments with X-rays. No attempt has been made to confine the exposure of the cloud-chamber to these rays to the period between the production of the super-saturated condition and the passage of the illuminating spark. Such photographs, therefore, show not only the sharply defined tracks of α- or β-particles which have passed through the super-saturated air after the expansion, but also diffuse double tracks in which the positive and negative ions have been separated by the electric field) due to ionising particles which have traversed the air before the expansion.

X-rays.—The source of radiation has throughout the work been an X-ray bulb of old type with a platinum anticathode. The rays were produced (in nearly all cases immediately after the sudden expansion of the air in the cloud-chamber) by the discharge of a large Leyden jar. To make the action of the X-ray bulb regular when used in this way a sufficient resistance had to be inserted in the circuit to make the discharge non-oscillatory. The maximum potential difference across the terminals of the bulb as measured by a spark gap was about 45,000 volts.

The bulb was generally placed with its anticathode at a distance of 46 cm. from the centre of the cloud-chamber and on the same horizontal level, and was surrounded by a thick lead case. A horizontal beam of X-rays, which passed through the centre of the cloud-chamber at right angles to the axis of the stereoscopic camera, was obtained by means of a horizontal lead tube attached to the lead case; the tube was 20 cms. long and was provided at each end with a thick lead diaphragm with suitable aperture. The form and area of cross-section of the beam could be varied by changing the diaphragms, and absorbing screens could be inserted at either end of the tube.

Photographs were taken of the cloud tracks when no screens were inserted (other than a thin mica window in the wall of the cloud-chamber) and with screens of thickness ranging up to more than 2 cm. of aluminium. For a satisfactory study of the β-rays produced by X-radiation it was necessary that their numbers should be kept comparatively small. When no screen was used a convenient number of β-rays was obtained by reducing the X-ray beam to a cylinder of about $0 \cdot 5$ mm. in diameter; when the thickest screens were inserted a square or rectangular beam of about $0 \cdot 5$ square cm. in cross-section was used. The effects of radiations of very different wave-lengths were in this way studied.

A number of experiments were made with the air at pressures considerably

less than atmospheric; the lowest final pressure used was about 10 cms. of mercury.

The experiments have thus far been confined almost entirely to air.

3. *Effects to be expected from the absorption of X-rays in air.*

According to the quantum theory, when X-radiation of definite frequency ν traverses the air of the cloud-chamber and is partially absorbed by it, it loses a certain number of quanta of energy each equal to $h\nu$. Each quantum absorbed by the air causes the ejection of an electron and is thus represented by a β-ray track in the cloud picture. Of the quantum of energy $h\nu$ absorbed by an atom, a part depending on the nature of the atom and the energy level from which the electron is ejected is used in removing the elctron from the atom, the rest is represented by the kinetic energy of the emergent β-particle. The velocities and therefore the ranges of the β-particles ejected by primary radiation of given frequency will thus not all be alike in a mixed gas, like air.

The air of the cloud-chamber contains, besides nitrogen and oxygen, other constituents in quantities sufficient to cause appreciable absorption of X-rays. From what is known regarding the absorption of X-rays we may deduce that the relative number of β-particles ejected by X-radiation of wave length λ from the K-levels of atoms of each of the different constituent elements of the air is approximately proportional to $Z^4\lambda^3N$, where Z is the atomic number and N is the number of such atoms per cubic centimetre of the air; this only applies if the frequency of the incident radiation exceeds the K-absorption limit, otherwise there is no K-absorption. Applying this we find that, while the absorption of X-rays by the hydrogen, carbon dioxide, neon, krypton and xenon present should be relatively negligible, about 60 per cent. of the β-rays which result from ejection of electrons from the K-level should be due to nitrogen, 25 to oxygen, 15 to argon. We should expect also a small number of β-particles to be ejected from the outer levels of atoms of these various elements.

The β-rays originating from these various sources under the action of X-rays of given frequency will have different ranges. When the frequency of the incident radiation is high the differences in the ranges of the β-rays will be unimportant. When, however, the frequency of the incident radiation is not many times that of the absorption limit of argon, as in the experiments with a copper target described in § 4, the range of the β-ray from the K-level of argon will fall far short of that from the K-level of an oxygen or nitrogen

atom; the difference between the ranges of the β-rays from the K-levels in oxygen or nitrogen atoms, or from the K- and L-levels in either of these atoms, also ceases to be negligible. We have in such a case a whole series of possible ranges for the β-ray tracks corresponding to the various lines in the magnetic spectrum in experiments such as those of de Broglie.*

The ejection of an electron from an atom by the action of the primary X-rays will in general be followed by the emission of secondary radiation. An atom from which a K-electron has been ejected will emit a quantum of one of its characteristic K-radiations. The K-radiation emitted may give evidence of its existence by ejecting an electron from the K-level of an atom of smaller atomic number or from the outer level of any atom. It would in this way be possible for K-radiation from argon to be absorbed by oxygen with ejection of an electron from the K-level and subsequent emission of oxygen K-radiation; this in turn might be absorbed in ejecting an electron from the K-level of nitrogen and thus causing the emission of nitrogen K-radiation; the final β-ray track will be that of an electron ejected from the outer level of an atom.

A ray produced in air by the action of primary X-rays may have no secondary β-ray associated with it, if it has itself been ejected from among the outer electrons of an atom; it may be expected to have a short range β-ray associated with it, if it has been ejected from the K-level of nitrogen, or it may have more than one if it has arisen in the K-level of oxygen or argon.

As will appear later, the matter is made more complicated by the combined effects of the primary and secondary radiations.

4. *Experiments with "targets" inserted in the path of the X-rays.*

In these experiments a small rectangular piece of metal foil, a few square mm. in area, was fixed at the centre of the cloud-chamber. It was attached to the flattened end of a needle, which projected vertically downwards from the centre of a brass plug closing a circular hole in the glass roof. A cylindrical beam of X-rays, about 0·5 mm. in diameter, was made to strike the centre of the target approximately at right angles.

Plate 1, fig. 1 shows the effects of inserting a copper target, about 8×10^{-3} cm. in thickness, in the path of the narrow pencil of X-rays. The various effects due to the absorption of the primary X-radiations by the copper are well shown. A large number of β-rays radiate from the target; the absence

* 'Journal de Physique,' vol. 2, p. 265 (1921).

of their initial portions is merely due to the heating and other disturbing effects of the copper.

Scattered about in the surrounding air outside the primary X-ray beam are to be seen numerous short β-ray tracks, due to electrons ejected by the secondary radiations from the copper. The greater number of these short tracks, ranging from 1·0 to 2·4 mm. in length in air at $\frac{2}{3}$ of atmospheric pressure, are due to the ejection, by the characteristic K_α and K_β-radiations of copper, of electrons from the different constituents of the air. Small, nearly spherical, clouds about 1/10 mm. in diameter, also appear—the tracks of the slow β-particles ejected by the L-radiations of copper.

Fig. 2, Plate 1, was obtained in an experiment in which the conditions were identical with those just described except that the X-rays had been cut down before entering the cloud-chamber by inserting in their path an aluminium screen 9·2 mm. in thickness. Here no β-rays have been produced by the direct action of the primary X-rays on the air. One β-particle has been ejected from the copper plate, and one β-ray track has been formed in the air, outside the X-ray beam, by the absorption of a quantum of K-radiation from the copper. To produce the quantum of K-radiation which has ejected the β-particle from an atom of oxygen or nitrogen an electron must have been ejected from the K-level of one of the copper atoms; the track of this one electron appears in the photograph. We almost certainly have here the tracks of the two electrons which are associated respectively with the emission and absorption of the same individual quantum of copper K-radiation.

A similar picture was obtained with a platinum target; the length of the β-ray ejected by the secondary radiation indicates that it is due to an L-radiation from the atom of platinum from which the primary β-ray was ejected.

Experiments were also made in which the primary X-ray beam and the target were outside the cloud-chamber. The target was an inclined metal plate placed immediately above an aluminium window in the centre of the roof of the cloud-chamber; a horizontal beam of X-rays was incident upon it. The photographs obtained with copper and silver targets showed well the different effects of the K-radiations from these metals.

The ranges of the β-rays produced in air by the K-radiations from copper varied between about 0·6 mm. and 1·7 mm., those produced by the silver K-radiations between 8 mm. and 16 mm. In both cases the tracks could be grouped into three classes according to their ranges; these classes correspond to the different lines in a β-ray spectrum. The range which recurred with

maximum frequency is (in accordance with the greater intensity of the K_α lines in the X-ray spectrum) taken to be due to the ejection of an electron from the K-level of an oxygen or nitrogen atom by the K_α-radiation from the metal; the group of maximum range is taken to be due to the ejection of an electron from the same elements by the K_β-radiation. The β-rays of shortest range produced by the K-radiations have probably been ejected from the K-level of argon atoms; their ranges are in accordance with this view.

The ranges of the β-rays ejected from oxygen or nitrogen by the K_α and K_β-rays from copper are about 1·3 mm. and 1·7 mm. respectively; those ejected by the K_α and K_β-radiations of silver have ranges of about 11 mm. and 15 mm.

Putting the kinetic energy of the ejected β-particle equal to the difference between the energy ($h\nu$) of the incident radiation and that required to eject an electron from the K-level of nitrogen we have in the case of the copper K-radiations, $K_\alpha\,(\mathrm{Cu}) - K\,(\mathrm{N}) = 7{,}700$ volts, $K_\beta\,(\mathrm{Cu}) - K(\mathrm{N}) = 8{,}600$ volts. Similarly the kinetic energies of the β-particles ejected by the silver K_α and K_β-radiations are 21,700 and 24,600 volts approximately.

The results of these measurements of the mean ranges of β-particles of different kinetic energies are represented approximately by the formula $V = 21{,}000\,R^{\frac{1}{2}}$, where V is the kinetic energy of the particle expressed in volts and R its range in centimetres, measured along the track, in air at atmospheric pressure. The experimental results are thus in approximate accordance with Whiddington's fourth-power law* connecting the range and velocity of a β-particle. The velocity of a β-particle of range 1·5 cm. is nearly $\frac{1}{3}$ of that of light and the kinetic energy given by the relativity formula.

$$m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right)$$

already exceeds $\frac{1}{2}m_0v^2$ by nearly 10 per cent.; for higher velocities the relation between range and kinetic energy is likely to be less simple.

The tracks of β-particles, such as those due to aluminium K-radiations or copper L-radiations, of which the kinetic energy is less than 2,000 volts are of too short range (less than 1/10 mm.) to be measurable; they appear in the pictures as small, nearly spherical, clouds.

5. *Different classes of β-rays produced in air by X-rays.*

When the air in the cloud-chamber is exposed to hard radiation—the wave-length of which is for example about 0·4 A°—three classes of β-ray tracks

* 'Roy. Soc. Proc.,' A, vol. 86, p. 360 (1912).

may be distinguished :—(*a*) "Long" tracks having a range of several centimetres; (*b*) "sphere" tracks, small, almost spherical, cloudlets, 1 or 2-tenths of a millimetre in diameter; and (*c*) tracks of 1 or 2 mm. in range, of which the initial direction approximately coincides with that of the primary X-ray beam. From their characteristic appearance when a number of them are present I have been in the habit of recording the tracks of this last class as "fish" tracks; the tail of the "fish" is directed towards the source. Figs. 3 and 4 contain examples of the three classes of tracks.

The "long" tracks are undoubtedly the paths of electrons ejected from atoms in most cases by the direct action of the primary beam, each having absorbed one quantum of energy corresponding to the frequency of the primary radiation. The range of these tracks depends on the frequency of the primary radiation and has been used for the purpose of estimating that frequency.

The "fish" tracks are also—as the direction of ejection indicates—almost certainly due to the direct action of the primary radiation; but the energy of the ejected electron is only a small fraction of that of a quantum of the primary radiation, and these tracks do not appear when the wave-length of the incident radiation exceeds 0·5 A°. They are almost certainly connected with the phenomena which have led Barkla and others to postulate the existence of a "J"-radiation; again to explain other phenomena relating to secondary radiations A. H. Compton has suggested the possibility of the forward ejection of short range β-particles.

"Sphere" tracks are probably in all cases merely the tracks of very short range β-rays; any β-particle with energy less than that corresponding to about 2,000 volts will produce such a track. Some of the sphere tracks which are formed in air exposed to X-rays of high frequency are probably produced in the same way as the fish tracks; intermediate comma-like forms are of frequent occurrence. Other sphere tracks are undoubtedly due to the ejection of electrons by secondary X-rays. A sphere track is frequently situated close to the origin of a long track and is sometimes outside the primary beam of X-rays. The ejection of the short range β-particle may in this case be due to the characteristic radiation from an atom, from the K-level of which the primary X-radiation has expelled the β-particle which produced the long track. There are, however, other cases of association of β-rays in pairs which cannot be explained so simply. (See section 8.)

6. *Direction of ejection of the β-particles.*

(*a*) *Polarisation.*—In almost every stereoscopic picture of the tracks of β-particles produced by a horizontal beam of X-rays, in which a convenient number (10 to 30) of tracks are present, several are found to start, as nearly as can be distinguished, in directions parallel to a vertical plane containing the axis of the X-ray beam. The cathode ray stream in the X-ray bulb was always directed vertically upwards, so that the vertical plane is that in which we should expect the electric vector in the polarised portion of the radiation to lie.

About 20 per cent. of the β-particles were found to be ejected in the vertical plane. Barkla found about 20 per cent. of the radiation from the X-ray bulb used by him to be polarised.

That a partially polarised beam of X-rays shows a deficiency of β-rays starting in directions lying in the plane of polarisation and an excess starting in direction lying in the perpendicular plane has been confirmed by some more recent experiments. In these a horizontal beam of primary X-rays was incident on a cylinder of paraffin wax placed above an aluminium window in the roof of the cloud chamber; a scattered beam partially polarised in the vertical plane passes vertically downwards into the cloud-chamber.

(*b*) *Forward component in velocity of ejection.*—In the photographs obtained in 1912 no systematic preponderance was evident in the number of β-rays which were ejected with a forward rather than a backward velocity relative to the direction of the X-rays which caused their ejection; this was perhaps mainly due to the tracks being too closely crowded together. Such a preponderance of β-particles which have a forward component in their initial velocity is a striking feature in most of the stereoscopic pictures which have recently been obtained, *e.g.*, fig. 6, Plate 5.

A study of individual tracks shows at once that the forward component in the velocity of a β-particle does not depend simply upon its velocity of ejection, *i.e.*, upon the wave-length of the radiation absorbed. The β-ray tracks may be divided into three easily distinguishable classes, according as the forward component is positive, zero or negative.

It is remarkable that quite a considerable proportion of the tracks belong to the 2nd class, *i.e.*, they are due to β-particles which have been ejected almost exactly at right angles to the X-ray beam. The tracks belonging to the first class, which is the most numerous, have in nearly all cases a comparatively large forward component, very frequently approximately equal to the lateral com-

ponent; *i.e.*, the most frequent direction of ejection makes an angle of about 45° with that of the X-ray beam. Fig. 3, Plate 2, contains examples of the two first classes in the centre of the picture. Again the third class consists mainly of β-rays with a backward component comparable with the lateral components. Cases in which there can be any doubt as to the class to which a β-ray is to be assigned are very rare.

The results of the examination of 1,148 tracks with regard to their initial direction are given in Table I.

Table I.

Average range (millimetres)	Energy kilovolts.	Total number of tracks.	Tracks with positive, zero and negative forward components.					
			Number in each class.			Number in each class per 100 tracks.		
			+	0	−	+	0	−
20–30	30–36	223	155	37	31	69	17	14
15–20	25–30	662	385	136	141	58	21	21
7–15	17–25	202	106	56	40	52	28	20
2–7	9–17	61	28	21	12	45	35	20

The last columns of Table I show very clearly that the percentage of β-ray tracks which have a forward component in their initial direction increases rapidly with increasing velocity and range of the ejected electron, *i.e.*, with increasing frequency of the incident radiation. This increase is mainly at the expense of the β-rays with zero forward component.

The difference between the effects of radiations of higher and lower frequencies on the average direction of ejection lies much more in the relative number of electrons which start with a forward component than in the direction of ejection of those which have the forward component. Tracks which have a forward component, even if their range is less than 1 cm., start most frequently in directions inclined at angles of about 45° to that of the X-ray beam. The forward inclination is in this case, it may be remarked, much larger than that deduced according to the view that the quantum of radiation absorbed passes on the whole of its momentum to the ejected electron.* On the other hand tracks of long range, 3 cm. or more, frequently start at right angles to the X-ray beam; or again their initial direction may have a larger backward component.

Tracks with a very large forward inclination are, however, mainly of long

* Richardson, 'Electron Theory of Matter.'

range. A few such tracks start almost along the direction of the X-rays; on the other hand a few long-range tracks start almost in the opposite direction, *i.e.*, towards the source of the X-rays.

In the above account of the phenomena relating to the direction of emission of the ejected β-particles it is to be noted that the special type of tracks in which the forward component in the velocity is most marked—the "fish" tracks—has not been included.

A thorough investigation of the direction of ejection of β-particles of all ranges with a fairly accurate measurement of the angles is likely to lead to interesting results.

7. *Short-range β-rays: "sphere," "comma" and "fish" tracks.*

The intensity of the ionisation in the final tenth of a millimetre of the range of an ordinary β-ray in air is so great, and the deviations so frequent and large, that its cloud track generally ends in a more or less spherical bunch or knot, consisting of drops too closely packed for resolution. Any β-ray of shorter range than about 1/10 mm. (*i.e.*, of energy rather less than that corresponding to 2,000 volts) is represented by a cloud track which consists of the sphere alone. If the range is slightly greater the initial portion of the track may show as a small tail projecting from the sphere; we thus get a comma-like track. If the range is a little longer the form of the track is such that, when a number appear together with their "tails" all pointing in one direction, they resemble a shoal of small fishes.

In air exposed to X-rays such "sphere" tracks and "fish" tracks together generally considerably exceed in number the long tracks, if the latter have an average range exceeding 1·5 cm. (figs. 3 and 4, Plates 2 and 3).

The fish tracks and comma tracks are absent, and the sphere tracks are relatively few, if the long tracks are all of range as short as 7 mm. (Fig. 5, Plate 4.)

When the frequency of the incident radiation is increased beyond a point where the ordinary β-ray tracks have a range of about 1 cm. the number of sphere tracks begins to increase rapidly and soon becomes comparable with that of the long tracks. With a further increase in the frequency of the radiation some of the spheres develop tails on the side next the source and become comma-shaped. When the X-rays are hard enough to eject β-particles of 1·5 cm. range, fish tracks of ranges up to about 0·4 mm. appear; their range increases as the frequency of the incident radiation is increased, but rarely exceeds 1·5 mm., even when the long tracks have a range exceeding 3 cm.

An estimate of the energy and frequency of the radiation absorbed in ejecting the electrons which produce the comma and fish tracks may be obtained from the ranges of ordinary β-particles ejected at the same time. It has, however, to be remembered that the incident radiations were far from homogeneous, so that the radiation absorbed in producing the fish tracks may have been of somewhat different frequency from that which corresponds to the mean range of the long tracks. But the data are sufficient to show that the difference between the energy of a quantum of the incident radiation and the kinetic energy of the ejected electron to which a fish track is due is between 20,000 and 30,000 volts; and that the maximum wave-length of the radiation consistent with the production of the fish tracks is between 0·4 and 0·6 A°.

It is just to this region of the spectrum that Barkla* and Crowther† have assigned the wave-length of the "J"-radiations, of which they found evidence in certain anomalies encountered in the study of absorption and scattering in elements of low atomic number.

Before it is concluded that there are electrons in the atoms of oxygen or nitrogen, of which the work of ejection is between 20,000 and 30,000 volts, or on the other hand, that this difference between the energy of a quantum of the incident radiation and that of the short range β-ray is represented by scattered radiation—in accordance with a suggestion made by Compton—some other possibilities must be considered.

It might in the first place be objected that the short-range β-tracks may be due to a constituent of correspondingly long wave-length remaining in the incident radiation. The two classes of tracks (of a range of several centimetres and of a fraction of a millimetre) obtained, for example, when the radiation has previously been filtered through 2 cm. of aluminium, or its equivalent in copper, tin or lead, might be due to the residual primary radiation and to the characteristic radiations from the screening material respectively. But the short range tracks are confined almost exclusively to the primary beam as defined by the two diaphragms at the ends of the collimating tube, whether the screen is placed between the X-ray bulbs and the collimating tube or between the collimating tube and the thin glass of the cloud-chamber. In the latter case the fluorescent X-rays should radiate in all directions from the screen, not only along the direction of the primary radiation. Again the nature and relative number of the short tracks was not found to depend on the material of the screen.

* 'Barkla, 'Phil. Trans.,' A, vol. 217, p. 315; 'Phil. Mag.,' vol. 34, p. 270 (1917).

† Crowther, 'Phil. Mag.,' vol. 42, p. 719 (1921).

The fish and comma tracks might also be attributed to the ejection of electrons from the K-levels of atoms of the rare gases of the atmosphere of higher atomic number, the relatively small number of which would be to some extent counterbalanced by the very rapid increase of absorption with increasing atomic number. The K-absorption limit of xenon falls not far below the lower limit found above for the effective wave-length. The number of the short-range tracks—which are approximately as numerous as the long tracks when the frequency of the incident radiation is high—is, however, far too great for this source to be a possible one.

A "fish" track or comma track is thus almost certainly due to the ejection of an electron from an atom of one of the common constituents of the air by radiation of the same frequency as that to which the long tracks are due. If a whole quantum of the incident radiation is absorbed in the ejection of an electron from an atom of oxygen or nitrogen, the electron must have come from an energy level below that of the K-electrons, the difference between this "J"-level and the K-level being represented by 20 or 30 kilovolts; *i.e.*, the electron must have been very closely attached to the nucleus.

There are great difficulties in the way of accepting the view that there is a "J" energy level in the atom, and that the difference between the kinetic energies of the electrons producing the long and short tracks respectively represents a difference in the energies required to remove electrons from the J and K energy levels. The fact that these short-range electrons are ejected very nearly in the forward direction is of itself sufficient to indicate that the process of ejection differs essentially from that of the ejection of the ordinary long-range electron.

To account for various phenomena relating to the wave-length and distribution of secondary X-rays A. H. Compton has suggested the possibility of just such a forward ejection of electrons as actually occurs in these "fish" tracks.

Compton* points out that if there is a type of scattering in which a whole quantum of radiation is dealt with by one electron of the atom, this electron may be expected to receive the whole momentum, $h\nu/c$, carried by the radiation. If we suppose that the scattered radiation is emitted by the electron in all directions—not localised in a bundle—then the electron will gain by the scattering process a momentum, $mu = h\nu/c$, in the forward direction and a kinetic energy $\frac{1}{2} mu^2 = \frac{1}{2} h\nu u/c$.

Let us suppose that it is only the K-electrons which are effective in this

* "Secondary Radiations produced by X-rays," 'Bull. Nat. Research Council,' Washington (1922).

type of scattering in elements of low atomic number like oxygen and nitrogen. There will then be no ejection of the electron from the atom unless $\frac{1}{2}mu^2$ exceeds the energy corresponding to the K-absorption limit—the equivalent of about 380 volts in the case of nitrogen. If we calculate the energy of the incident radiation $h\nu = cmu$ corresponding to this value of $\frac{1}{2}mu^2$ we obtain $h\nu = 19{,}800$ volts. This may be regarded as giving the calculated minimum energy of the radiation which is required to produce rudimentary "fish" tracks; at this stage such a track would be represented by a single pair of ions. Similarly 28,000 volts would give to the scattering electron twice the energy required to eject it from the atom, and a typical "sphere" track would result; about 50,000 volts would be required to give a properly developed "fish" track.

The agreement between the observed phenomena and these applications of Compton's theory lends strong support to that theory. It is a question of great interest whether the quantum of radiation scattered by an electron is emitted in all directions (with a continuous wave front) as assumed above, or in one direction only as Compton suggests. In the latter case the direction and magnitude of the resultant momentum of the electron will depend on the direction in which it emits the radiation.

Information on this very fundamental question may possibly be obtained from a more thorough study of the initial directions and ranges of the fish tracks produced by homogeneous radiation of known wave-length.

Many of the sphere tracks which appear in the path of a beam of hard X-rays are almost certainly of the same nature as the fish tracks; they are merely of too small range to show any "tail."

Others, however, are plainly the tracks of electrons ejected by the K-radiations emitted by atoms from which an electron has been ejected by the primary beam. They may occur outside the primary beam; they are frequently situated close to the origins of other tracks, forming one component in several of the classes of paired β-ray tracks considered in the next section.

8. *Association of β-ray tracks in pairs or groups.*

The β-ray tracks produced in air exposed to X-rays very frequently occur in pairs or groups. The association in pairs or groups may be of any one of the following types:—

(1) A long-range track and a short-range track start from the same point.

(2) One, or sometimes two or more, short-range tracks, generally sphere tracks, appear close to the origin of a long-range track.

(3) Two short-range tracks form a pair without any long-range track being associated with them.

(4) Two long-range β-ray tracks, generally similar in range, have their origins near together.

(5) Two long range tracks start from the same point.

It is, of course, only when the tracks are not too closely packed that it becomes possible to distinguish some of the above types of pairing. Unless the average distance apart of the origins of the tracks exceeds considerably the distance apart of the components of a pair, the relationship of the members of a pair will not generally be obvious.

That the association in pairs or groups is real and not accidental is, I think, made sufficiently clear in the photographs which have been reproduced. Fig. 7, Plate 6, contains examples of types (1), (2) and (5).

Class (1). *A long-range track and a short-range track from the same point.* (Figs. 8, 9 and 17, Plates 7 and **11.**)

About 20 per cent. of the "long" β-ray tracks which have been produced by hard X-rays in air at pressures not differing much from atmospheric show distinct indications that a very short-range β-ray starts from the same origin. In some cases there is merely an enlarged head to the long β-track, no larger than some of the beads which occur along the course of the track; but very frequently the short-range track has a range of 2 or 3-tenths of a millimetre and shows quite distinctly as a lateral projection of the origin of the long track. At lower pressures the short tracks are of easily measurable length. In air at a pressure of 10 cm. of mercury many of these initial lateral tracks are from 1·5 to 2 mm. in length. A large proportion start approximately at right angles to the long track, but other very different angles, larger or smaller, occur. In several cases the short track is along the direction of the primary X-ray beam, like a "fish" track.

Even at the lower pressures a long-range track may show at its origin merely a bead (sometimes wholly or partially resolved into drops) to indicate the emission of the short-range β-ray. The effect of very short-range β-particles is more easily detected at low pressures, and it is probably mainly in consequence of this that a larger proportion of long tracks (about 30 per cent.) have at such pressure been recorded as showing the initial short-range track.

It is possible that in many cases the two particles have been ejected from the same atom, the β-particle which produces the short-range track having been ejected by the faster electron in the course of its escape. On the other

hand the origin of this type of pairing of β-ray tracks may be essentially the same as that of the other types (classes 2, 3 and 4) in which the two β-particles do not come from the same atom.

Class (2). *A long-range track with short-range track close to its origin.* (Figs. 10, 11, 12 and 18, Plates 8, 9, and 11.)

When air is exposed to X-radiation of sufficiently short wave-length to produce β-rays exceeding about 15 mm. in range, about 30 per cent. of these have short tracks associated with them, but starting from separate origins; the origins of the long and short tracks are generally at distances varying from a small fraction of a millimetre up to several mm. in air at 50 mm. pressure. The long track of such a pair may or may not have a short track starting from its origin and forming with it a pair of the first class.

There can be little doubt that in some cases the short track of a pair of the second class is due to a β-particle, ejected from a second atom by the action of the K-radiation of the atom from which the faster β-particle was ejected. The K-radiations from oxygen or nitrogen would give rise to β-rays of ranges indistinguishable from these sphere tracks. There are frequently two, sometimes even three, or more, short tracks associated with a long one. Some cases of this kind may represent the handing-on of energy from atom to atom of successively lower atomic number; *e.g.*, the β-ray which gives rise to the long track may come from the K-level of an oxygen atom, which then emits its K-radiation; this may eject an electron from the K-level of a neighbouring nitrogen atom. The β-particle thus ejected from nitrogen would only have sufficient energy (about 100 volts $= O_K - N_K$) to set free a small group of ions; the nitrogen atom will in turn emit its K-radiation which may be absorbed in ejecting an outer electron from a neighbouring atom. The sphere tracks are as might be expected, on this view of different dimensions, and some of the smaller which have been resolved only contain about 10 pairs of ions.

The above explanation gives, however, by no means a complete account of the phenomena, and can in fact apply only to a relatively small number of cases of this type of pairing. In a narrow beam of soft X-rays only a small proportion, not exceeding two or three per cent. of the ordinary β-ray tracks are accompanied by sphere tracks (other than those which appear as beads on the β-ray tracks themselves); and such sphere tracks as do occur are as often as not outside the primary X-ray beam. The above explanation may apply in the case of these soft X-rays; the photographs show, however, that the greater number of the quanta of K-radiation emitted by the gas exposed

to the primary beam must under these conditions either escape beyond the volume of air under observation before ejecting an electron and producing a sphere track or they are absorbed in the long β-ray tracks themselves.

With X-radiation of frequency sufficient to produce β-rays of 15 mm. or more in range, the proportion of those which have sphere tracks associated with them is greatly increased; the increase in the number of sphere tracks is confined almost entirely to the air lying within the primary X-ray beam. A sphere track outside the primary beam, like that in the lower part of Fig. 17, is quite rare. If the pressure is reduced they still remain within the primary X-ray beam while the average distance of each from its associated long-range track increases.

The effect of reducing the pressure shows that for the production of both the long and short components of a pair, the direct action of the primary beam is in general essential. This is also shown in a striking way when the X-ray beam is given the form of a narrow vertical sheet; the two components have then their origins very nearly in the same vertical plane.

If, as is probable, one of the components of a pair is primary and the other secondary, the secondary radiation from the point of origin of the primary β-ray is thus shown to be much more likely to eject a β-particle from an atom exposed to the primary X-rays than from one lying outside the primary beam.

The short track associated with the long one is not always a simple sphere track; its range may be sufficient to give it the comma-shaped or fish-like form. When of this form it is generally directed approximately along the direction of the X-ray beam in the same way as an independent "fish" track (figs. 12 and 18, Plates 9 and 11); it may, however, be directed with its "tail" pointing towards the origin of the longer track.

When the short track is of the simple sphere form, its most frequent situation relative to the origin of the long track is along a perpendicular to the initial direction of the long track (fig. 10, Plate 8).

When two short tracks are associated with a long track they may both be alike, and may form an obvious pair, or they may be quite unlike in range and orientation. The "long" track of fig. 12, Plate 9, has apparently two pairs of short tracks associated with it; one pair consists of two similar spheres, the other of a sphere track and a "fish" track.

Class (3). *Two separate short-range tracks.* (Figs. 13-16, Plates 9 and 10.)

Short-range tracks, other than those associated with the same long track also frequently occur in pairs. About 40 per cent. of such tracks belong to pairs.

Most frequently the pair takes the form of two sphere tracks. (Fig. 14, Plate 10.) A fish track is, however, frequently accompanied by a sphere track or by another fish track. (Figs. 15 and 13, Plates 10 and 9.)

There is a tendency for the points of origin of the two components of a pair to lie nearly on a line perpendicular to the axis of the X-ray beam. (Figs. 12 and 13, Plate 9.) One of the components—a sphere track—may lie outside the primary beam, but this is exceptional.

Experiments on the effects of varying the form and area of cross-section of the beam of X-radiation and the pressure of the air led to results similar to those which were found to hold for the previous class of pairs. If one of the components of the pair of β-rays is to be regarded as primary the other as due to radiation from the atom from which the primary β-particle has been ejected; then to explain the experimental results we must conclude that this secondary radiation is much more likely to eject a β-particle from an atom exposed to the primary radiation than from one lying outside the primary beam.

When the primary beam was a cylindrical pencil 0.5 mm. in diameter the average distance of the components of a pair was about 0·5 mm. in air at 50 cm. pressure. In a wide beam distances up to 5 or 6 mm. occurred, the mean distance exceeding 2 mm., and there was a much greater tendency for the two components of a pair to have their origins in a line nearly perpendicular to the axis of the X-ray beam; the frequency of occurrence of pairs as compared with single short-range tracks was also increased.

Class (4). *Two long-range tracks from neighbouring points.* (Figs. 21 and 22, Plate 12.)

A considerable proportion of the long tracks (*i.e.*, of all tracks other than sphere, comma and fish tracks) occur in pairs. In a wide beam of hard X-rays (of wave-length less than 0·5 A°) about 40 per cent. of such tracks were found to be paired. The proportion of paired tracks was smaller, not much exceeding 20 per cent. in a narrow beam of soft radiation in which all the tracks were less than about 7 mm. in range. In such a beam as has already been pointed out fish tracks are absent and sphere tracks few.

Both members of a pair are, with very rare exceptions, within the primary X-ray beam. In a wide beam their average distance apart amounts to

2 or 3 mm. in air at 50 cm. pressure. There is, as with pairs of the preceding class, a great tendency for the line joining the points of origins of the two members of a pair to be nearly perpendicular to the primary X-ray beam.

In a narrow beam, the average distance apart is diminished, as is to be expected if both components originate within the primary beam; it is frequently about 0·5 mm. in a cylindrical beam of 0·5 mm. diameter. The line joining the origins of the two members of a pair is also in general much less inclined to the axis of the X-ray beam than in a wide beam.

At low pressures the average distance apart of the origins of the members of a pair is increased, and thus the two components of the only pairs which appear—since both rays in general start within the primary beam—have their origins in a line making only a small angle with the axis of the X-ray beam.

As with the two preceding classes of pairs, when the X-ray beam has the form of a narrow vertical sheet, the two members of a pair nearly always lie in almost the same vertical plane. This is perhaps the most striking proof that the direct action of the primary X-rays is involved in the production of both members of a pair.

Groups of three or even more long β-rays sometimes occur, but much less frequently than pairs. In a wide beam there is, as with a pair, tendency for all the members of such a group to have their points of origin in the same plane, nearly perpendicular to the primary beam.

Class (5). *Two long-range tracks from the same point.* (Figs. 19 and 20, Plate 11.)

The emission of two long-range β-rays from the same point (or from points too near for resolution in the stereoscopic pictures) is not uncommon. Cases of the emission of three and even of four β-rays from the same point have been noticed. These may all possibly form merely a particular case of the preceding class in which the two electrons have been ejected from molecules which are too near together for resolution. But in practice they form quite a distinct class. It seems, moreover, quite natural to suppose that, when the conditions for absorption are suitable, the radiation from an atom should have a specially great chance of being absorbed by the same atom or by another atom of the same molecule.

The number of cases of two long tracks originating from the same point as compared with the whole number of cases of paired long tracks is greatest in a narrow beam of X-rays traversing air at low pressure. Of the whole number of pairs of long tracks about one-third consist of two from the same

point in a 0·5 mm. beam at a pressure of about 15 cm. This is in accordance with the view that the two components of the pair originate in the same molecule. For the chance of absorption by an atom of the same molecule as that in which the quantum of secondary radiation is emitted remains unaltered by lowering the pressure or narrowing the beam, while the total number of other molecules available for absorption is proportional to both the air pressure and the cross section of the beam.

There is a tendency for the two members of a pair of long β-rays, whether they originate at the same or neighbouring points, to be similar in range, and in the angles which their initial directions make with the axis of the primary beam of X-rays. A striking example is that of fig. 22, Plate 12.

Two long tracks from the same or neighbouring points may be accompanied by associated short tracks. For example, in fig. 20, Plate 11, a typical "comma" track is associated with two long tracks and another short track, the last three apparently starting from the same point.

9. *Time interval between the ejections of the two components of a pair.*

Owing to the fact that a resistance was inserted in the circuit, each discharge of the Leyden jars through the X-ray bulb lasted an appreciable time—about 0·01 second. During this time the nature of the X-rays emitted may have varied much in wave-length, polarisation and otherwise. Thus the tendency of the two β-ray tracks of a pair to be similar might be interpreted as meaning that the β-particles were ejected so nearly simultaneously that the radiations effective in the ejection of both were similar in character. Some of the photographs were taken under conditions such that the expansion occurred during the X-ray discharge, so that, while some of the tracks were sharp, others (due to β-particles ejected before the expansion was completed) were wholly or partially separated by the electric field into positive and negative diffuse tracks. In such a picture, in accordance with the above explanation, a pair may occur in which both components are sharp, while nearly all the other tracks are diffuse, or diffuse when most of the other tracks are sharp.

What is somewhat unexpected is the appearance in such pictures of what seem undoubtedly to be pairs, in which one component is sharp and the other diffuse; *i.e.*, pairs of which the two components have been ejected with an appreciable time interval. A rough estimate can be made from the vertical separation which the positive and negative ions of the diffuse tracks suffered before being fixed; it is of the order of 1/1,000 of a second.

10. *On the origin of the paired tracks.*

In Section 5 evidence was brought forward to show that X-rays of sufficiently short wave-length in traversing air cause the ejection of two classes of β-particles which differ greatly in range; the difference in their kinetic energies generally corresponds to more than 20,000 volts. Let us suppose that as a result of ejection of the electron and consequent re-arrangement of the remaining electrons there follows in both cases the emission of a quantum of K-radiation from the atom.

The K-radiation from an atom of nitrogen in the absence of other influences is not able to eject an electron from the K-level of a second atom of nitrogen. The phenomena relating to the paired tracks suggest that such an atom, when exposed to the K-radiation from a similar atom, together with radiation of higher frequency, is able to absorb both radiations (with ejection of a K electron) much more readily than either separately. Let us suppose that the ejection of the electron by the primary X-rays, whether it occurs with or without the help of the K-radiation, may be either of the type which gives the long-range β-particle or of that which gives the short-range forward-directed β-particle. Then all the various types of pairs—all possible combinations of long and short β-ray tracks—may be accounted for.

In the case of an element of low atomic number like nitrogen, it is perhaps not impossible that the K-radiation, while not able of itself to eject an electron from the K-level of a similar atom, may be absorbed in transferring the electron to an outer level, and that the K-radiation may be then re-emitted and handed on from atom to atom like ordinary resonance radiation. The occasional occurrence of a time interval of the order of 1/1,000 of a second between the ejection of the primary and secondary β-particles is perhaps more easily understood on this view.

Summary of Results.

Many hundred stereoscopic pictures showing the number, distribution, direction of ejection and range of the β-particles emitted from atoms in air exposed to X-rays have been obtained and examined. The following are some of the conclusions to which a study of the photographs has led.

(1) The cloud-method is able to deal with individual quanta of radiation, in the sense that the track of the electron ejected from the atom which emits the quantum of radiation and that of the electron ejected from the atom which absorbs the radiation may under suitable conditions be identified.

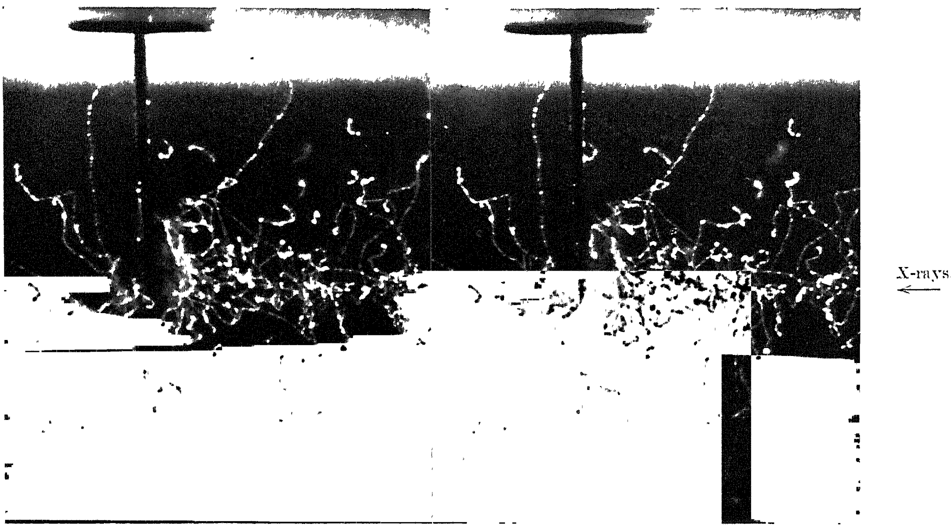
(2) Two classes of β-ray tracks are produced in air by the primary action of X-radiation of wave-length less than about 0·5 A°—(*a*) those of ejected electrons with initial kinetic energy comparable to a quantum of the incident radiation, and (*b*) tracks of very short range. The short range electrons are ejected nearly along the direction of the primary X-rays. Their direction and range and the value of the minimum frequency of the radiation which is required to produce them are in agreement with the suggestion made by A. H. Compton, that a single electron may be effective in scattering a quantum of radiation and that in so doing it receives the whole momentum of the quantum. The short-range tracks are probably related to the phenomena which have led to the postulation of a "J"-radiation.

(3) The ordinary long-range tracks may be divided into three classes according to the direction of ejection of the electron. The majority have a large forward component comparable with the lateral component; a considerable proportion, of the order of 20 per cent., are ejected almost exactly at right angles to the primary X-ray beam; others have a large backward component.

(4) Partial polarisation of the primary beams is indicated by the direction of ejection of a number of the β-particles being in one plane—that containing the direction of the cathode rays in the X-ray tube.

(5) β-rays in air exposed to X-rays frequently occur in pairs or groups, of which five classes have been distinguished. The pairs probably consist of one K-electron ejected by the direct action of the primary X-rays, and of a second electron ejected by the combined action of primary radiation and of the K-radiation from the atom from which the first electron was ejected.

Fig. 1 (×2).



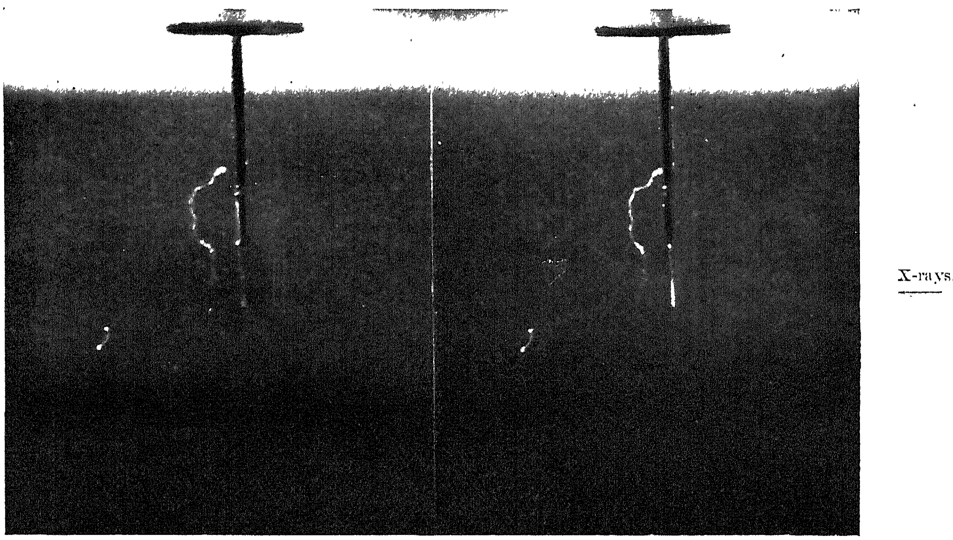


FIG. 2 (×2).

Experiments with copper target (Section 4). Diameter of cylindrical X-ray beam 0·5 mm. Thickness of copper plate 8×10^{-3} cm. Final air density about 0·7 normal. In (2) aluminium screen, 9·2 mm. thick, was interposed.

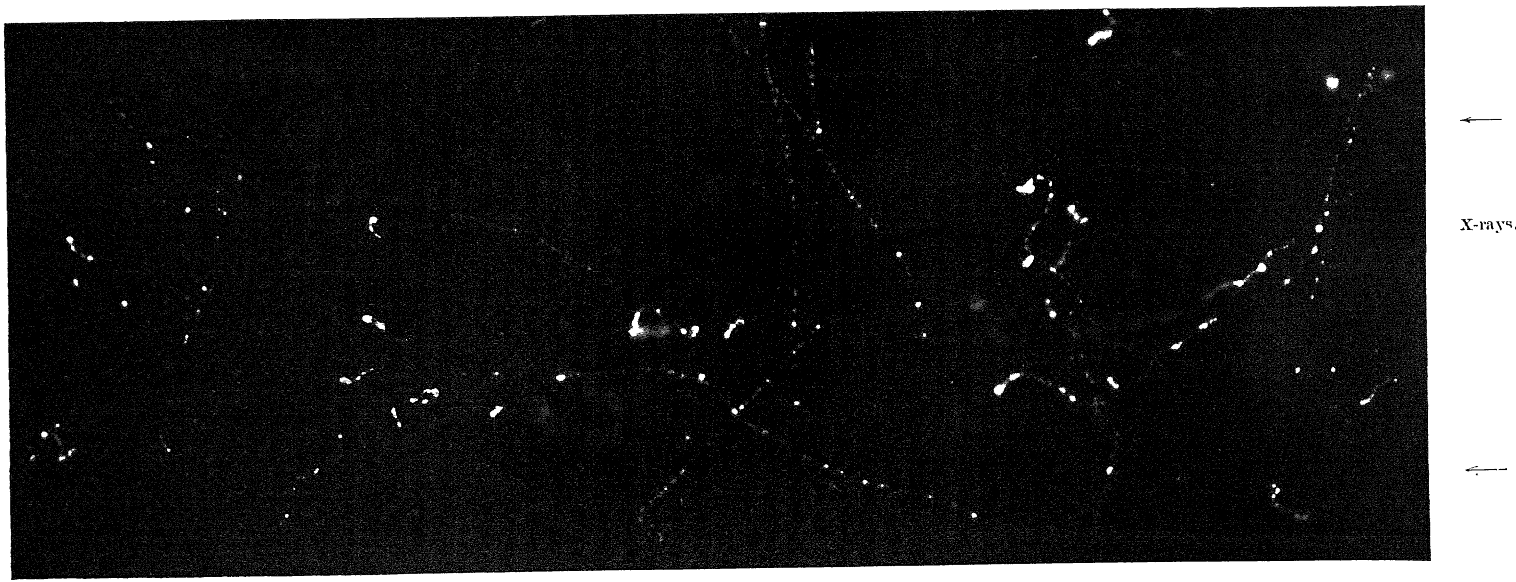


Fig. 3 (×3).

Effects of hard X-rays: (1) production of long-range and short-range β tracks, (2) forward direction of the "fish" tracks, (3) long tracks at right angles to X-rays, others with large forward component.

X-ray beam 15 × 4 mm. in section, filtered through 14 mm. of aluminium.

Final air pressure 20 cm.

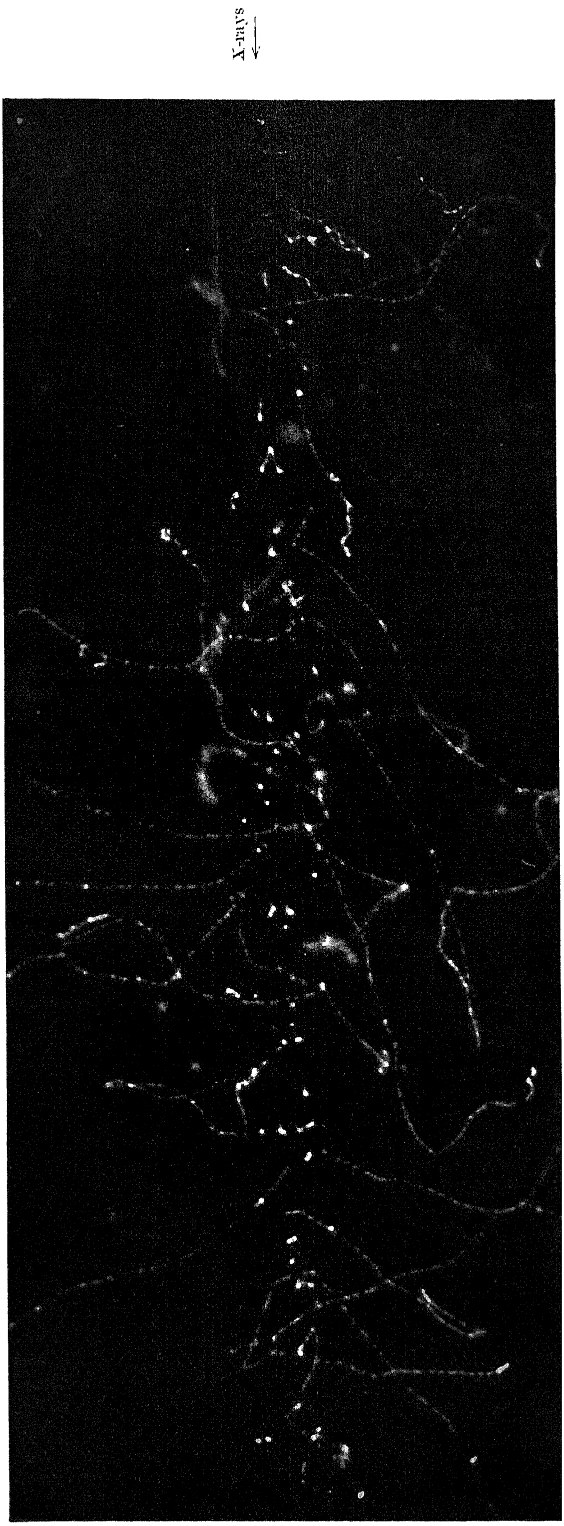


Fig. 4 (×3).

Different classes of β-ray tracks, "long," "fish," and "comma" tracks produced by hard X-rays. Initial forward component in long tracks. X-ray beam, about 3 mm. in diameter, had traversed 6×10^{-3} cm. lead. Final air pressure 50 cm.

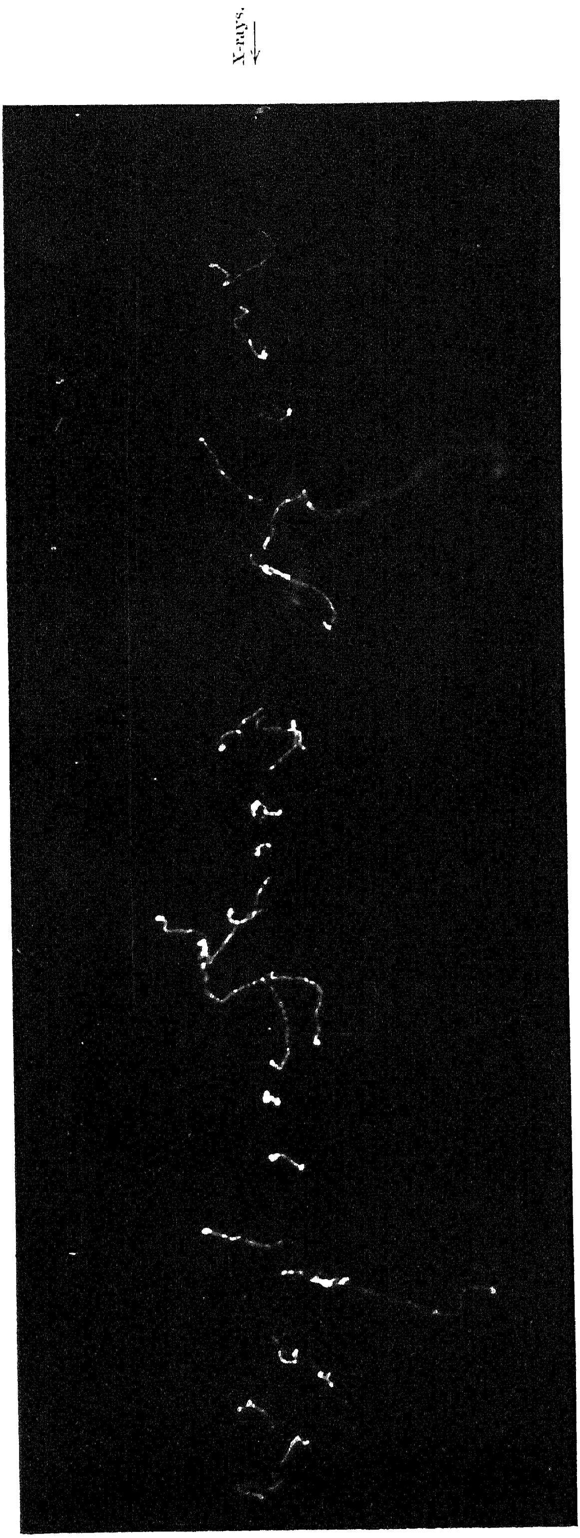


FIG. 5 (×3).

Narrow cylindrical beam of soft X-rays. Sphere tracks and fish tracks absent. Diameter of X-ray beam 0·5 mm. Final pressure 50 cm.

X-rays.

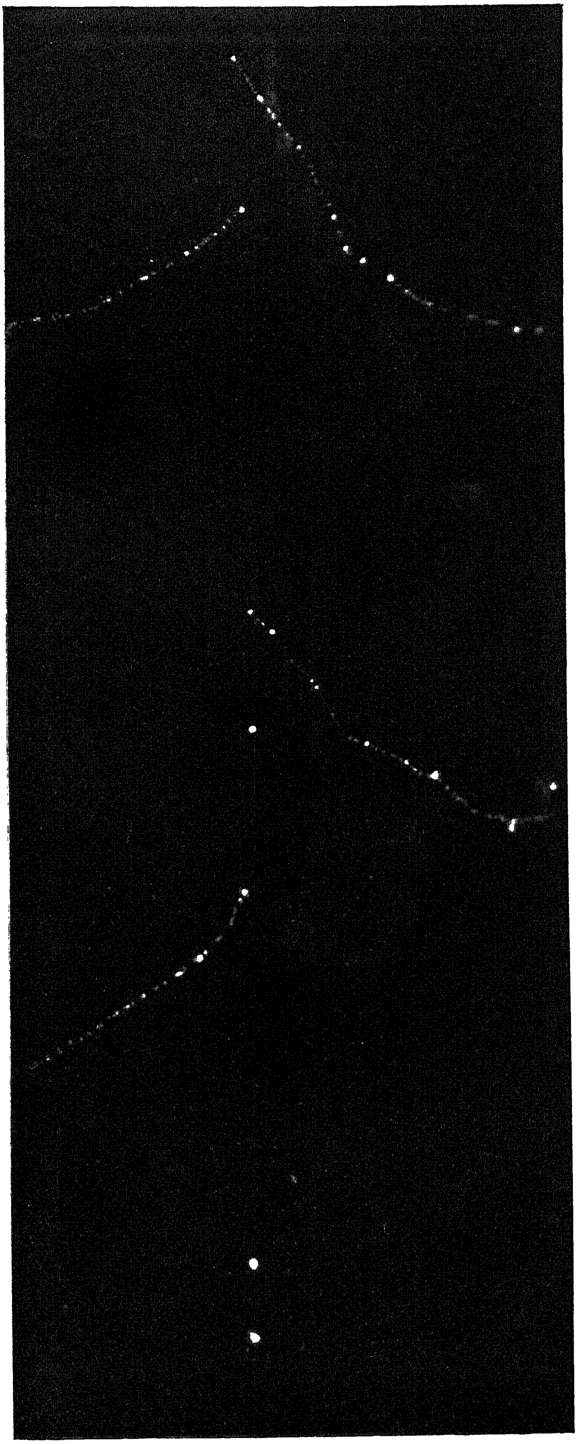


FIG. 6 (×3).

Long tracks with large forward component. Sphere tracks. Cylindrical X-ray beam, 0·5 mm. in diameter, has traversed 8×10^{-3} cm. copper. Final pressure 19 cm.

X-rays.

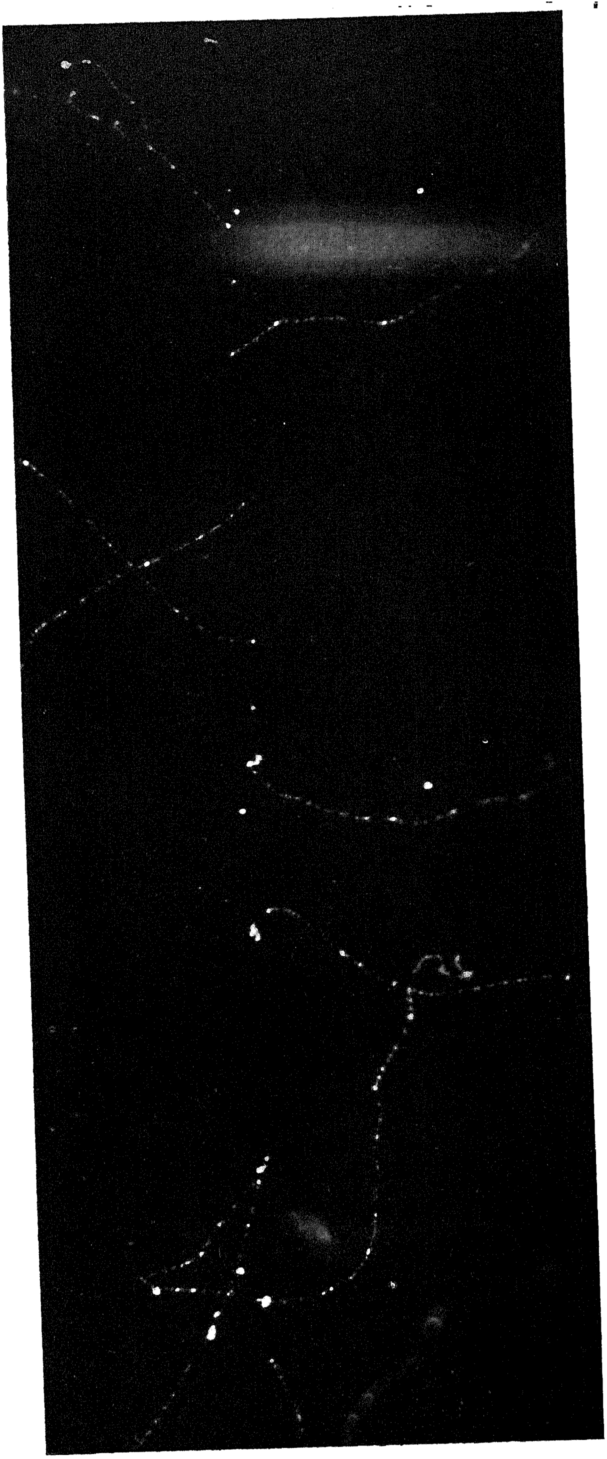
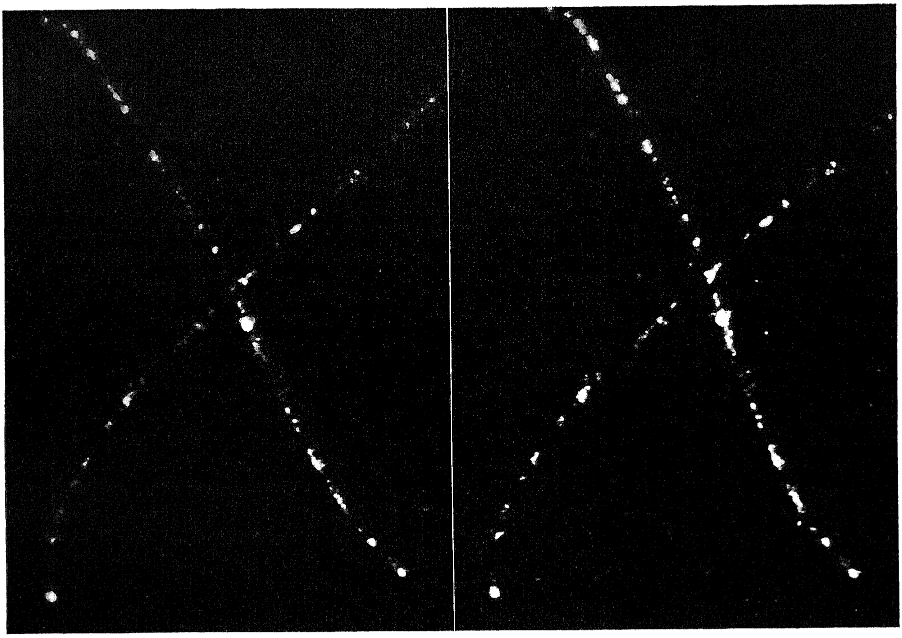


FIG. 7 (×3).

Different types of pairs. The branched track on the right has a sphere at its origin and another near it. At the left of the picture two long tracks start from the same point. Other long tracks have sphere tracks associated with them. One long track has large initial backward component. Cylindrical X-ray beam, 0·5 mm. in diameter, had traversed 2·9 mm. aluminium. Final air pressure 20 cm.

Fig. 8 (×8).



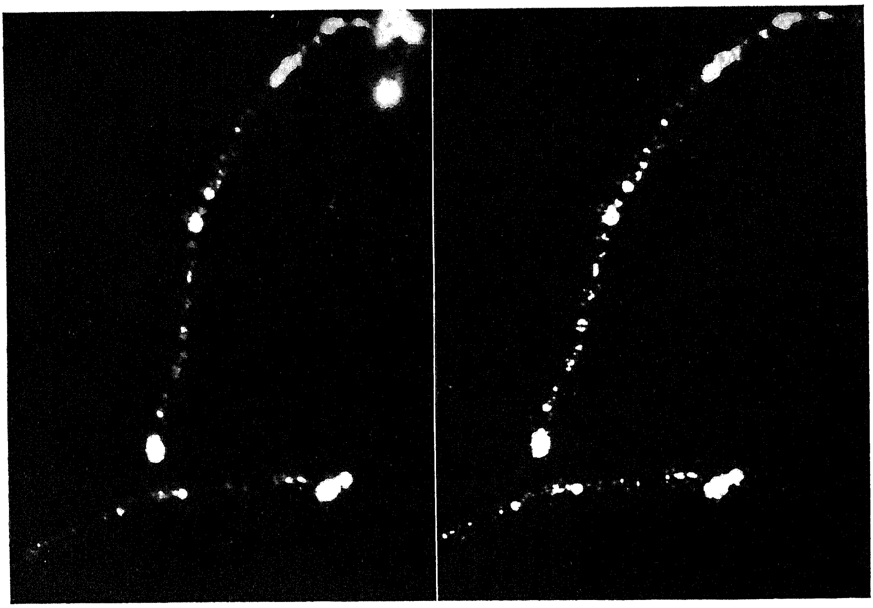


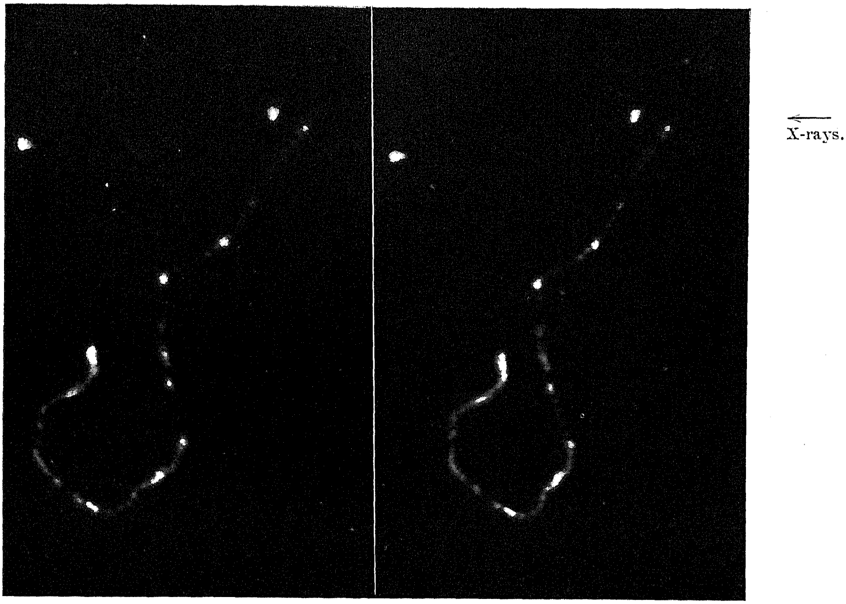
Fig. 9 (×8).

Paired tracks of type 1 (Section 8).

Fig. 8.—Two long tracks from Fig. 7.

Fig. 9.—Final air pressure 19 cm.

FIG. 10 (×8).



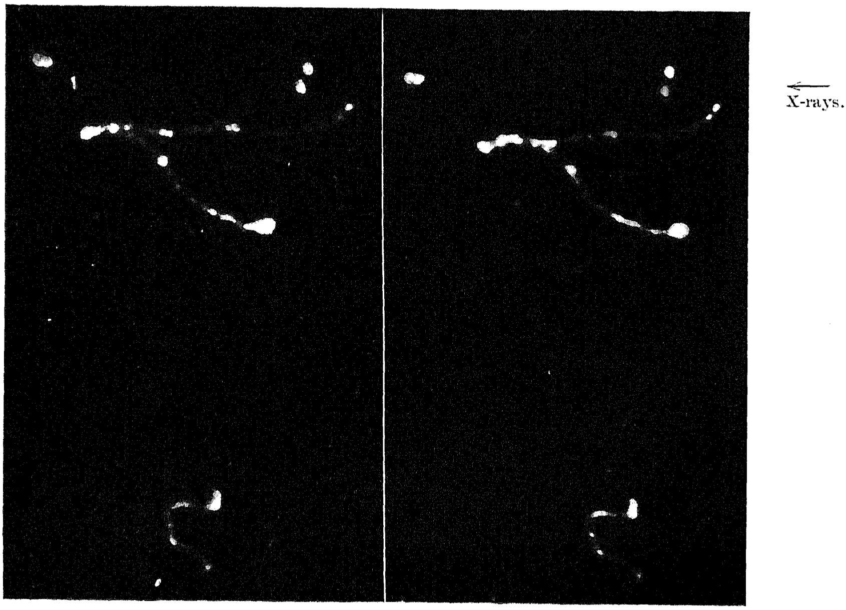
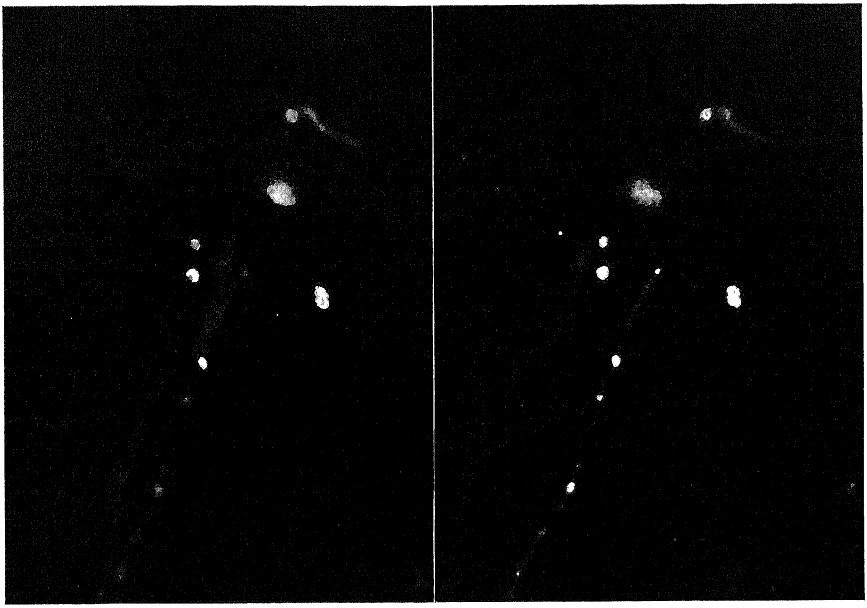


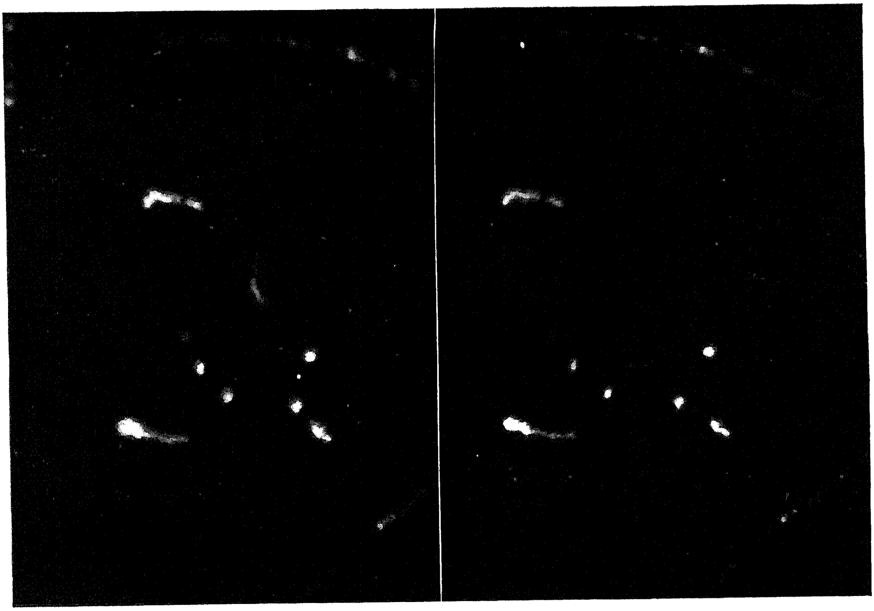
FIG. 11 (×8).

Paired tracks of type 2 (Section 8).
Final pressure 53 cm.

FIG. 12 (×8).



X-rays.



X-rays.

FIG. 13 (×8).

FIG. 12.—Long track with associated short tracks. Final pressure 50 cm.
FIG. 13.—Paired fish tracks and group of sphere tracks. Final pressure 50 cm.

FIG. 14 ($\times 8$).

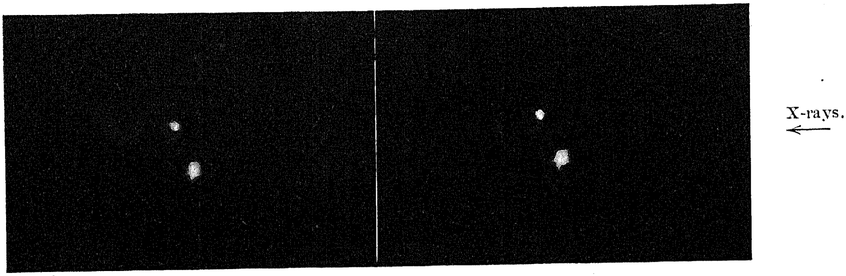


FIG. 15 ($\times 4$).

FIG. 16 ($\times 4$).

FIG. 14.—Paired sphere tracks. Final pressure 20 cm.

FIG. 15.—Fish track and associated sphere track. Final pressure 19 cm.

FIG. 16.—Associated fish tracks (from Fig. 3).

X-rays.

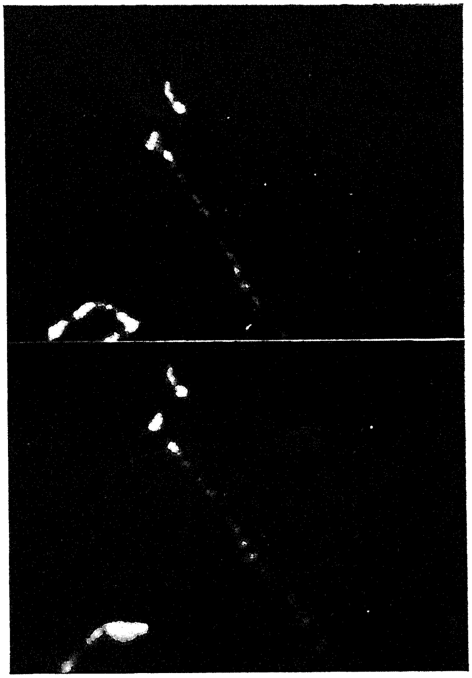


FIG. 18 (×4).

X-rays.

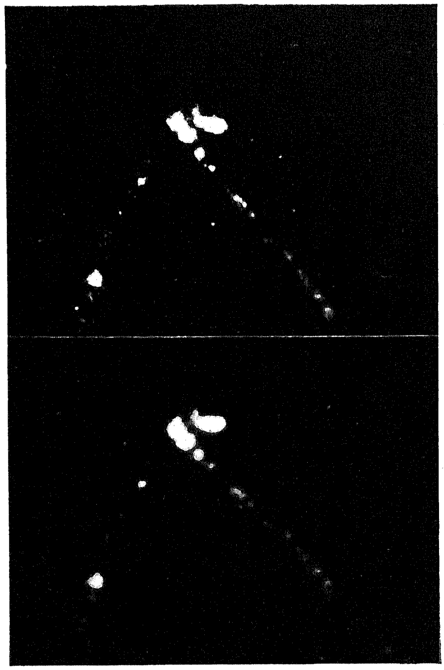


FIG. 20 (×8).

X-rays.

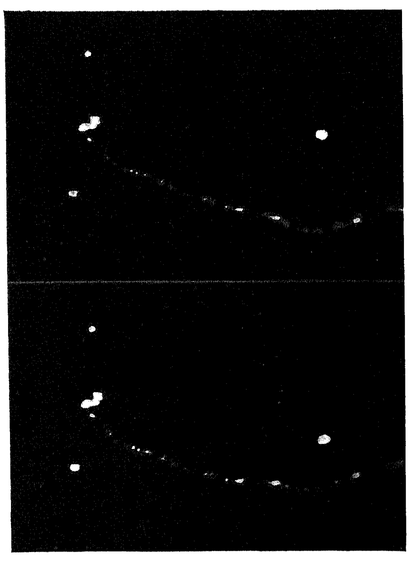


FIG. 17 (×4).

X-rays.

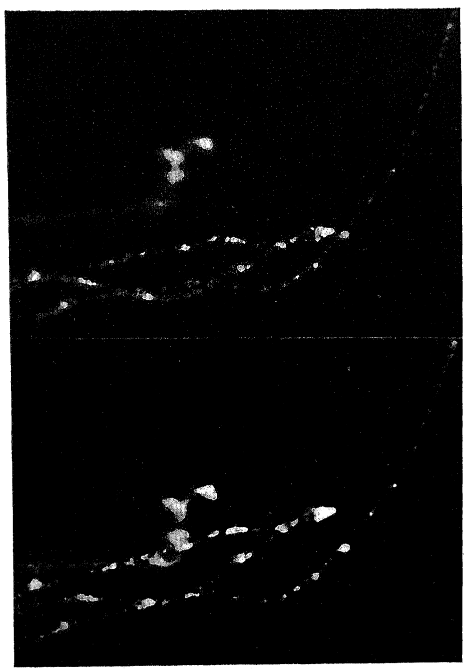


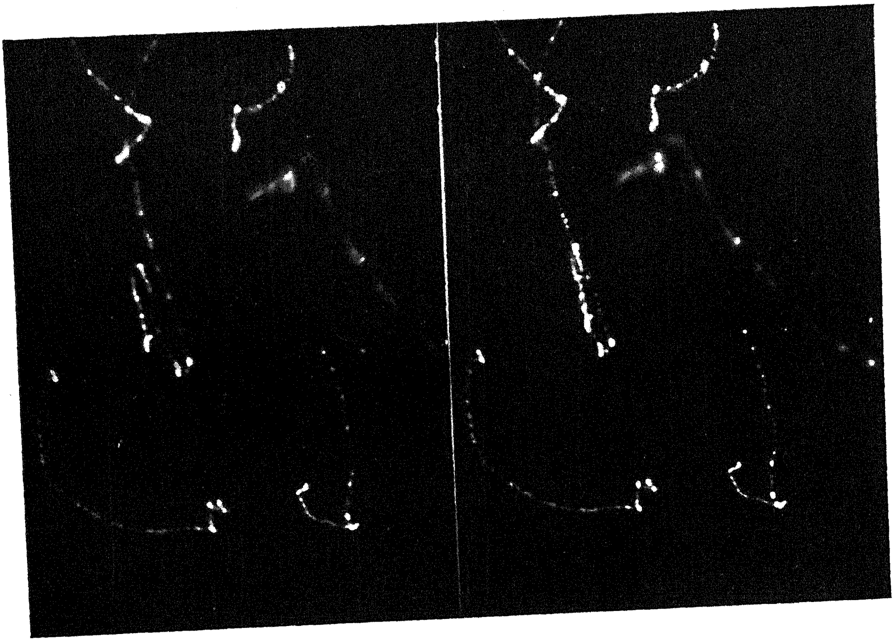
FIG. 19 (×4).

Associated Tracks.

FIGS. 17, 19, 20.—Final pressure 20 cm.

FIG. 18.—Final pressure 50 cm.

FIG. 21 (×4).



X-rays.

X-rays.

FIG. 22 (×4).

Paired long tracks (Section 8).

FIG. 21.—Final pressure 55 cm.

FIG. 22.—Final pressure 50 cm.

Boundary Lubrication.—The Latent Period and Mixtures of Two Lubricants.

By W. B. Hardy, F.R.S., and Ida Doubleday.

(A Report to the Lubrication Committee of the Department of Scientific and Industrial Research.)

(Received June 20, 1923.)

Part I.—The Latent Period.

When a lubricant is applied to a solid surface the friction, with certain definite exceptions, does not at once reach its steady value, but starting from a relatively high level, falls in longer or shorter time to a constant value. The existence of this latent period has been known to us for a long time and put aside for further enquiry, the values of μ considered in the earlier papers having always been the final or "steady" values.

The latent period seems to be merely the time occupied in the orientation of the molecules of the lubricant at the solid face.

The carbon chains of fatty acids or alcohols are loaded at one end with the —COOH or —OH groups respectively. They may, therefore, be likened to rods loaded at one end. Placing a pool of fluid upon a surface is like flinging at it a handful of such rods grasped at random. Some will hit and stick by the loaded ends, others by the unloaded ends. The rods may be supposed to be attracted to the solid more strongly by their loaded ends, and the process of evaporation into the overlying fluid and condensation from it will increase the proportion of rods sticking to the solid face by their loaded ends until a steady state is reached. The steady state will not be one in which all the rods of the primary film have their loaded ends directed inwards, since, in the give-and-take with the overlying fluid, some of those condensing are likely to arrive unloaded end foremost. The steady state will, in short, be an average state depending upon the rate of evaporation and condensation, and upon the difference between the attraction of the solid for the loaded and unloaded ends respectively.

Similar considerations hold when the primary film is formed by condensation from vapour, but then the rods are flung singly.

Let us suppose that a steady state has been reached for both slider and plate, for example by exposing both to the saturated vapour of the lubricant, and let the slider then be placed on the plate. There now are two primary

films enclosed between two solid faces and, therefore, shielded from evaporation or condensation. If the molecules of these films still possessed sufficient freedom of movement to effect end for end changes, a further latent period would be observed with further fall in friction until the final steady state was reached in which all the molecules were oriented with loaded ends attached to the solid faces. This seems to happen, and it explains the fact, which was at first so puzzling, that the lowest steady value of friction can be got with fatty acids and alcohols only by leaving the slider for some time in position on the plate.

The proof that this view of the latent period is correct lies in one significant and striking fact, which seems to us to be open to no other interpretation. It is that molecules composed of a chain of carbon atoms, both ends of which are alike, do not manifest a latent period. Normal paraffins are such substances. In their case the rods are unloaded, and no matter how applied to the surfaces the first recorded value of the friction is the same as the last.

The latent period must be of importance in practical lubrication, for it measures the rate of repair of the lubricating film. It is true that the object of the engineer is to keep lubrication within the limits of complete fluid lubrication, in which the solid surfaces are separated by a layer thick enough to exclude boundary conditions. But he rarely succeeds, since every particle of metal worn away is evidence of failure. Disaster happens in the region of boundary lubrication, and there the rate at which a ruptured or partly ruptured primary film can reform itself must be no unimportant factor.

The phenomena of the latent period, as they first presented themselves to us, were discouragingly complex. This could not be otherwise, because there are three possible steady states, namely, equilibrium with fluid, equilibrium with vapour, and the equilibrium of primary films enclosed between two solid faces, and the attempt to measure the value of the friction in either of the two first states causes it at once to begin to change to the third, because it necessitates placing the slider in position on the plate. All that can be done, therefore, is to take a reading of friction as quickly as possible, and regard it as an approximation to the value required.

There are three possible states and there are four variables which affect the duration of the latent period, namely, the chemical nature of the lubricant and of the solid faces, temperature, and mechanical agitation such as is produced by moving the slider about upon the plate.

Material, glass throughout. Figures are for the coefficient of friction μ, and the latent period is given in minutes.

Case I. A large pool of lubricant placed on the plate and the slider put into it at once.

—	First reading.	Steady value.	Latent period.
			Minutes.
Caprylic acid	0·57	0·34	60
Heptoic acid	0·50	0·40	45
Octyl alcohol	0·59	0·52	15

Case II. Surfaces in equilibrium with fluid lubricant before being placed in contact.—The slider and plate were covered with lubricant in excess and left in the chamber for three hours. The slider was then put on the plate, of course without opening the chamber.

—	First reading.	Steady value.	Latent period.
			Minutes.
Caprylic acid	0·26 rising rapidly to 0·44	0·34	10
Heptoic acid	0·31 rising rapidly to 0·46	0·40	10
Octyl alcohol	0·47 rising rapidly to 0·54	0·52	10

The first recorded value taken as soon as possible after the slider has been placed on the plate is low, and there is a rapid initial rise in friction: this is characteristic of surfaces which have been allowed first to come into equilibrium with the *fluid* lubricant.

These two cases taken together show that the condition of the lubricant is profoundly changed by contact with the solids, and we picture the sequence of events as follows:—

When a pool of one of these lubricants is placed on a solid, the molecules throughout have at first that random arrangement of the fluid in mass which confers upon it its characteristic viscosity. Orientation begins at once at the solid face and, as the primary film is formed, extends inwards into the overlying fluid until finally a steady state is reached of orientation maximal at the solid face and decreasing thence as it is more and more upset by the heat motions.

The orientation in the layer over the primary film will alter the viscosity, tending to increase it, and, therefore, the slider will take a sensible but brief time to squeeze out the excess fluid, until only the two primary films remain. Therefore, the first recorded value will not be for the primary film but for a layer of lubricant thicker than this, and the friction is lower than that given by completely oriented primary films. When the slider is placed in position

at once, that is before orientation has had time to become established, the excess fluid is squeezed out so rapidly that the first reading records the high friction of the imperfectly oriented primary films.

Experiments with glycerol confirm this view. This substance has a high viscosity in mass and, when used as a lubricant, the first readings of friction are vanishingly small. They rise, however, with lapse of time so that in an hour or so the friction has risen to the value for the clean unlubricated surfaces. Glycerol indeed, like water, is a neutral substance for glass and steel in that it does not lower static friction, but, owing to its high viscosity, considerable patience is needed to detect the fact.

If the initial low value of friction be the reading taken whilst the slider is sinking through fluid whose molecules are partly oriented, and whose viscosity is thereby greatly increased, then it should not be observed when the surfaces before being placed in contact are in equilibrium not with fluid, but with vapour. This is Case III.

Case III. Surfaces in equilibrium with the vapour of the lubricant before being placed in contact.—Saturated vapour was passed for three hours into the chamber, in which were both plate and slider but not in contact. Slider then placed on plate. The initial low value is not now observed.

—	First reading.	Steady value.	Latent period.
			Minutes.
Caprylic acid	0·45	0·34	5
Heptoic acid	0·48	0·40	5
Octyl alcohol	0·54	0·52	5

It will be noticed that the first reading for surfaces in equilibrium with fluid and with vapour respectively is, within the limits of unavoidable error (the state being in process of change after the slider is put on the plate), the same. As the friction is, *ex hypothesi*, a measure of the degree of orientation, we conclude that primary films in equilibrium with fluid are in the same state as those in equilibrium with vapour.

In what follows the latent period given is the time which elapses between putting the slider on the plate as soon as possible after lubrication and the attainment of the final steady state. Agitation, either thermal or mechanical, shortens the latent period. The effect of temperature is illustrated by the following figures which give the time required to reach the steady state after the slider has been placed in a pool on the plate.

Temperature.	Latent period.	First recorded value of μ.
	Heptoic acid on glass ($\mu = 0 \cdot 405$)	
	Minutes.	
15° C.	45	0·50
48° C.	15	0·46
72° C.	5	0·44
	Octyl alcohol on glass ($\mu = 0 \cdot 517$).	
	Minutes.	
13° C.	30	0·59
50° C.	10	0·55
60° C.	2 to 3	0·53

The value of μ *in the final steady state* is independent of temperature, within the limits of accuracy of the experimental method (' Proc. R.S.,' A, vol. 101, p. 487 (1922)), as perhaps might be expected since the primary films are then sheltered from evaporation and condensation. The variation in the first recorded value of μ, that is, in the friction taken as soon as possible after the slider is in position, indicates, however, that the degree of orientation at surfaces *still in contact with fluid or vapour* does vary with temperature.

Mechanical agitation, such as is produced by moving the slider backwards and forwards on the plate, has a remarkable effect. For example :—

Slider in pool of caprylic acid.

Slider at rest.	Latent period	60 minutes.
Slider moved up and down the plate	,, ,,	10 ,,

Equilibrium is hastened and the latent period thereby shortened by movement of the slider, even when the solid surfaces are covered only by an insensible film, as the following example shows :—

The slider was resting on the plate in the chamber, and both were clean. A small drop of caprylic acid was then placed near one corner of the plate. In one hour the acid had spread over the surfaces, to cover them with an invisible but complete primary film, and the co-efficient of friction had fallen to the steady value $\mu = 0 \cdot 34$. The slider was then lifted quickly to another part of the plate when a reading taken as rapidly as possible gave $\mu = 0 \cdot 41$. The slider was then moved about this part of the plate, when the value fell almost at once to $0 \cdot 34$ and remained constant—that is to say, movement of the slider did not lead to any further change. The slider was then lifted

to another part of the plate and left quietly in position, when μ fell to its steady value 0·34 in 10 minutes.

It is to be observed that the sliders used had a spherical surface of radius 14·7 cm. The area of contact, therefore, was so small as to make it practically certain that, in spite of precautions which made the rocking insensible, the application of the external force did cause the slider to rock insensibly to a new contact. The effect of the slider in sheltering the primary films from evaporation into vapour or liquid is, therefore, probably not confined to the area of contact.

The properties of mixtures of lubricants belong to the next section. It will, however, be convenient to notice here the effect on the latent period of the presence of indifferent molecules—that is, of molecules which by themselves do not manifest the phenomenon. Water is an indifferent substance—indeed, it is a neutral substance in that it does not alter the friction of clean plates of glass on steel. Normal paraffins also are indifferent substances. In both cases the greater the relative number of indifferent molecules the shorter is the latent period. This is an entirely unexpected relation, because the indifferent molecules might be expected to interfere with the rate of evaporation and condensation of the active molecules.

Lactic acid and water on glass.

Clean value $\mu = 0·92$. Initial value of μ in *all* cases about 0·8.

Percentage of water.	Latent period in minutes.	Final value of μ.
100	0	0·92
99·59	5	0·67
74·4	20	0·62
21·4	30	0·57
1·7	45	0·56
0·0	60	0·55

Caprylic acid and Octane on glass.

Initial value of μ between 0·5 and 0·6 in each case.

Percentage of acid.	Latent period in minutes.	Final value of μ.
0	0	0·65
0·0007	0	0·65
2·05	2	0·34
15·59	3	0·34
39·89	5	0·34
99·08	40	0·34
100·0	45	0·34

When an alcohol and an acid are mixed the latent period is longer the greater the percentage of alcohol.

For example, in a mixture of octyl alcohol and caprylic acid.

Percentage of alcohol.	Latent period in minutes.
98·24	40
0·58	75

The practical interest of the latent period has been noted.

The theoretical interest lies in the proof it furnishes of the view put forward by one of us in 1913 ('Roy. Soc. Proc.,' A, vol. 88, p. 330) that orientation extends mathematically from any interface on both sides to infinity, but that its sensible extension is fixed by the heat motions which tend to upset it, and, we must now add, the righting forces on atoms in a crystal. This sensible extension is the "range of attraction" in the classical theory of capillarity and not the range of atomic or molecular attractions in a space otherwise empty of matter.

Part II.—Mixtures of Two Lubricants.

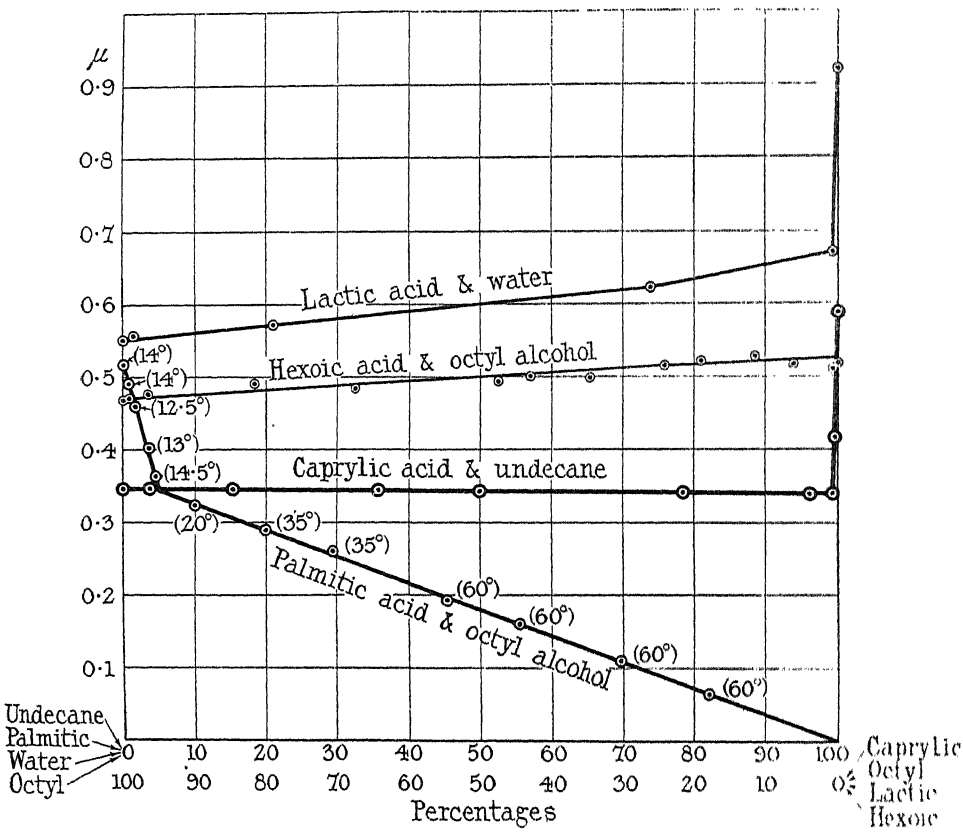
Save for casual reference, boundary lubrication with a single pure chemical substance has alone been considered so far in these papers. We now turn to a preliminary study of lubrication with two substances. The examples fall into two classes, that in which the lubricants were miscible and mixed before being applied, and that in which the lubricants whether miscible or not were applied successively. The object of the second series was in the main the study of the effect of the presence of two primary films upon each solid surface. It may be well to note here that when a single substance is used as lubricant the solid faces are separated by two primary films; whereas in the case just mentioned where two primary films dissimilar in character have been deposited upon both surfaces, these latter when opposed are at least potentially separated by four primary films.

The following facts, set out in detail later, prove, in our opinion, that when two immiscible substances such as a paraffin and water are applied in succession to each face and the faces then placed in contact, there actually are four films between the solid faces. When water vapour is admitted to a surface which is already covered by a film of a lubricant *miscible with water*, this film is disorganised and the friction thereby raised: but when the lubricant

is *immiscible with water*, the admission of water vapour always lowers friction. The disposition in this second case, namely, of superposed films, is, however, unstable and readily broken up, with rise of friction, by mechanical agitation.

I.—Lubricants mixed before being applied.

Examples of all the forms of curves discovered are gathered together in the figure. There are three types.



Type I.—For all mixtures of aliphatic acids or alcohols with a paraffin. The curve for the pair undecane and caprylic acid is chosen as the example.

Obviously, the acid or alcohol is condensed from the solution on to the surface so that, save when less than about 0·7 per cent. is present, the friction is the same as that for the pure acid or alcohol. The mixture cannot, however, be considered, *quâ* lubricant, as the equivalent of the pure acid or alcohol. It may be better or worse according to circumstances. The latent period of

the mixture is, for example, shorter, and, therefore, the rate of repair of the primary film greater.

The form of the curves suggests that there is a critical point in the dilution of the better lubricant, below which it can maintain a primary film formed completely of its own molecules, and above which the film includes molecules of both species.

These cases conform to the rule that the better lubricant is the one more strongly adsorbed by a surface, and, therefore, the one which most reduces the potential of the forces of attraction. If they were the only cases, the whole theory of boundary lubrication might rest securely on that basis.

Type II.—For mixtures of aliphatic acids and alcohols whose coefficients of friction when pure differ greatly (palmitic acid and octyl alcohol), and for lactic acid with water. The curve shows a critical point at which its direction suddenly changes, but there is no horizontal portion. Throughout the whole range of concentration the worse interferes with the action of the better lubricant. Some factor intervenes to restrain adsorption of the more active component.

Type III.—For mixtures of aliphatic acids and alcohols whose coefficients of friction do not greatly differ. There is no change of direction and no sign of preferential adsorption, the curve being a straight line.

Comparison of these three types shows that the form of the curve is not a simple function of the difference of level at the ends as it would be if boundary lubrication were determined wholly by adsorption. It is possible that the degree of miscibility of the components in the primary film is a factor, just as two components may be miscible as fluids but immiscible in the same crystal.

It should be mentioned that these curves are isotherms, except that for the mixture of palmitic acid with octyl alcohol. Owing to the limited miscibility of these substances it was necessary to raise the temperature as the proportion of acid was increased. The figure in brackets gives the temperature at which a measurement was made. It will be noted that there are no breaks in the curve corresponding to the changes of temperature.

It must be observed that the three types of curves given are not the only ones. In the course of this work many instances have been met when a lubricant has been applied to the faces in solution in a volatile solvent in which, as the last traces of solvent have been in process of evaporation, momentary values have been recorded much lower than the friction of the better lubricant when present alone. This is not shown in any of the curves

possibly because the effect is confined to so narrow a range of concentration as to have escaped notice.

II.—Lubricants applied in succession.

Pairs only were examined of which either water or benzene formed one.

Water, considered as a lubricant, is of a remarkable character. It is neutral to clean surfaces of glass or steel in that it neither lowers nor raises the friction. Glycerol, which in its physical characters is so akin to water, is another neutral substance, but considerable patience is needed to demonstrate the fact, owing to the high viscosity and, therefore, the time required for the fluid to flow away from between the faces. Water is neutral not because it is not adsorbed by the surfaces, and therefore the same may certainly be said of glycerol. Water vapour, for example, will not only condense to form an insensible film, but such a film is not displaced by any good lubricant, save with the help of mechanical agitation. Why water and glycerol should be neutral is quite obscure.

Water is a lubricant to other solids, even those whose surfaces it will not wet. For example, water will not wet a freshly exposed surface of solid paraffin, yet water vapour will condense on to the surface to form an invisible primary film which, as the following shows, lowers friction.

A glass slider coated with the solid paraffin $C_{24}H_{50}$ on a freshly prepared surface of the same paraffin:

In dry air	$\mu = 0 \cdot 060$.
Water vapour admitted	$\mu = 0 \cdot 025$.
Slider in a large pool of water	$\mu = 0 \cdot 025$.
Slider in a small drop of water	$\mu = 0 \cdot 11$.

The last two values of μ are given to illustrate a source of error, namely, that due to capillarity. The work needed to force water in mass over a surface it does not wet, such as that of a paraffin, *in spite of the fact that this is covered by an insensible film of water,* is great enough to be readily detected when a small drop of water is used, for the contour of such a drop is varied by the least motion of the slider.

Water vapour also condenses on to surfaces already covered by an insensible primary film of other lubricants, and the effect is to lower friction if water is immiscible with the lubricant, and to raise friction if the contrary is the case. The disposition in the former case is that of two primary films on each

face, the upper being of water, for the arrangement is unstable and readily broken up by the mechanical agitation due to moving the slider about.

Let us suppose the slider to be on the plate and the faces separated by four primary films, and let those films next the solids be called the outer films. Then, no matter whether water form the inner or outer pairs, the effect of the inner pair is always to lower friction below what it would be if the outer pair came together. In other words, a film of water deposited on a film of a lubricant immiscible with it lowers friction, and a film of an immiscible lubricant deposited on one of water also lowers friction. This may be of the nature of a general law. Many pairs will have to be studied before the effect of mechanical agitation on these doubled films is understood. All that can be done here is to point out the paradoxical results.

When water forms the inner pair of films, moving the slider about raises friction to a steady value which, however, is never the "clean" value; the value, that is, of water alone. The new steady value is reached much more quickly if the lubricant conjoined with water is fluid. In other words, if the outer pair are formed from a solid lubricant the system is more stable than when they are of a fluid lubricant.

When water forms the outer pair the effect of mechanical agitation might be expected to lower friction by permitting access of the lubricant to the solid surfaces. In fact it raises friction.

When the lubricant is miscible with water and present on the surfaces only as an insensible film, the admission of water vapour to the chamber always raises friction, and mechanical agitation by moving the slider about does not contribute to the effect.

Glass

Pure lubricant.		Water vapour admitted.
Lactic acid	$\mu = 0\cdot49$	$\mu = 056$
Ethylene glycol	$\mu = 0\cdot506$	$\mu = 0\cdot53$
Triacetin	$\mu = 0\cdot35$	$\mu = 0\cdot72$

Flooding the surfaces with water still further raises the friction, *e.g.*, in the case of ethylene glycol to $\mu = 0\cdot83$. This again, however, is not the value for water alone, which is that of clean glass, namely $\mu = 0\cdot92$.

When the lubricant is immiscible with water, and present as a film only, water vapour always lowers friction. Mechanical agitation now raises friction above the value for the pure lubricant.

Glass.

Pure lubricant.		Water vapour admitted.
Oleic acid	$\mu = 0 \cdot 31$	$\mu = 0 \cdot 17$
B.P. paraffin	$\mu = 0 \cdot 34$	$\mu = 0 \cdot 24$
Undecyl alcohol	$\mu = 0 \cdot 44$	$\mu = 0 \cdot 33$
Undecoic acid	$\mu = 0 \cdot 15$	$\mu = 0 \cdot 13$
Dimethyl decyl carbinol	$\mu = 0 \cdot 41$	$\mu = 0 \cdot 37$

The effect of moving the slider vigorously up and down the plate raised the value for undecyl alcohol + water from $0 \cdot 33$ to $0 \cdot 48$.

The following are solid lubricants :—

Tetracosane	$\mu = 0 \cdot 32$	$\mu = 0 \cdot 11$
Cetyl alcohol......	$\mu = 0 \cdot 32$	$\mu = 0 \cdot 09$
Palmitic acid	$\mu = 0 \cdot 0$	$\mu = 0 \cdot 06$

In all these cases water formed the inner pair of films. The reverse arrangement was obtained by placing the slider in a pool of a lubricant which, owing to its low vapour pressure was known not to spread as a primary film over the rest of the surfaces (see 'Roy. Soc. Proc.,' A, vol. 100, p. 573 (1922)). Water vapour was then admitted and the friction read first *within* the pool, and then the slider carrying part of the pool of lubricant with it was moved gently to another part of the plate which was covered with an insensible film of water.

Lubricant alone.		On surface already covered with film of water vapour.
Oleic acid (imp.) ..	$\mu = 0 \cdot 31$*	$\mu = 0 \cdot 62$
B.P. paraffin ..	$\mu = 0 \cdot 34$	$\mu = 0 \cdot 73$

In both these cases the full rise of friction was obtained only by moving the slider about, and, indeed, in the second case there was no rise of friction until this was done. The only possible interpretation of this is that B.P. paraffin lubricates the composite surface of glass covered by a film of water as well as it does a clean glass face, the only difference being that the succession of films is unstable to mechanical agitation, and that, when broken up, the new arrangement is less effective as a lubricant.

The question naturally arose in the course of these experiments whether the clean face of glass, seeing that water is used to cleanse it, is not already covered by a film of water. All that can be said in reply is that no procedure

* This is higher than the value for pure oleic acid. The impurity present seemed to consist in an acid of lower molecular weight.

which suggested itself to us altered the frictional properties of the face. The most drastic treatments were boiling in absolute alcohol and drying in dry air; or, after boiling in absolute alcohol, heating in an oven to 150° C. and cooling in dry air.

When there is only one pair of primary films between the solids the plane of slip may reasonably be assumed to be between them, that is, midway between the solid faces. When there are four primary films the matter is more dubious, since there are now five surfaces of discontinuity. The initial slip which defines the value of static friction is probably confined to the median surface or one of the other pairs of surfaces, because the yield point is not likely to be the same for surfaces which are differently placed; for example, the yield point of a surface between the two primary films of water, supposing water to form the inner pair, is not likely to be the same as that between water and the lubricant, or between the lubricant and the solid. The probability is still in favour of the median plane being the plane of slip, because the presence of an inner pair of primary films lowers friction. If this probability be granted then the figures prove that the attraction field of the solid is transmitted through *two* primary films to this plane.

Benzene, unlike water, lowers slightly the friction of substances even when it is miscible with them. This is not because benzene itself is a lubricant; indeed it is so nearly a neutral substance for glass as to lead one to attribute the very slight lubricating effect to an impurity, especially as very few samples of benzene, and those only after most tedious purification, will give the low lubricating value recorded below, namely:—

Clean glass .... $\mu = 0 \cdot 92$
Lubricated with benzene .... $\mu = 0 \cdot 89$

The admission of the vapour of this benzene gave the following results:—

—	Alone.	Saturated benzene vapour admitted.
Dimethyl decyl carbinol	0·41	0·39
Lactic acid	0·49	0·48
Cetyl alcohol	0·32	0·30
Tetracosane ($C_{24}H_{50}$)	0·325	0·316
Palmitic acid	Not measurable.	Not measurable.

Summary.

1. When the lubricant is composed of molecules whose structure is a chain of carbon atoms loaded at one end by a carboxyl or hydroxyl group, some time

elapses after its application to the solid surfaces before the friction reaches a steady state. This interval is called the latent period.

2. The latent period seems to be the time required to attain that degree of orientation of the molecules in the primary film possible under the particular circumstances. When, therefore, the lubricant is a normal paraffin in which both ends of the chain of carbon atoms are alike, there is no latent period.

3. The latent period is shortened by rise of temperature, by mechanical agitation, and by dilution with a substance such as a normal paraffin which itself does not manifest a latent period.

4. The lubricant consisting of two pure substances mixed together :—

(*a*) for aliphatic alcohol or acid mixed with a paraffin, the friction is identically that of the alcohol or acid until its percentage has fallen to about 0·7 :

(*b*) for a mixture of an aliphatic alcohol with an acid, the difference in lubricating properties being considerable the friction rose slowly with increase in the percentage of the worse lubricant until a critical point was reached, at about 5 per cent., when the curve bent sharply upwards.

Lactic acid and water conformed to this type :

(*c*) when the difference in lubricating properties was slight, the curve was a straight line joining the values of the coefficient of friction for the pure substances.

5. When two substances were applied to the faces in succession then :—

If the substances were immiscible the application of a second lubricant in the form of vapour always lowered friction.

If the substances were miscible, when water was the second to be applied, it always raised the friction ; when the second lubricant applied was benzene it always slightly lowered friction.

Mechanical agitation such as is produced by moving the slider on the plate raised the friction when two immiscible lubricants had been applied in succession to the surfaces.

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On a Class of Transcendents of which the Bessel Functions are a Particular Case.

By Major P. A. MacMahon, F.R.S.

(Received May 2, 1923.)

1. The transcendent is

$$E_{n,m}(z) = \sum_{r=0}^{\infty} \frac{(-)^r z^{n+rm}}{2^{n+rm}(r\,!)^{m-1}\,(n+r)\,!}$$

wherein, for the moment, we take n, m to be integers.

This becomes a Bessel coefficient when $m = 2$.

$$E_{n,2}(z) = J_n\,(z).$$

$E_{n,m}(z)$ has first and second orders, n, m, respectively.

Before dealing with the properties of the transcendent, a short account is given of the manner in which it has presented itself.

1.1. It became necessary, in combinatory analysis, to find the sum of the *different* coefficients which occur in the expansion of a multinomial

$$(\alpha_1 + \alpha_2 + \alpha_3 + \dots + \alpha_k)^m$$

wherein n is a positive integer.

The expansion can be exhibited as the sum of a number of symmetric functions. What we require is the sum of the coefficients of these functions.

The ordinary multinomial theorem gives, for $k = \infty$,

$$(1)^n = \Sigma \frac{n\,!}{(p_1\,!)^{\pi_1}\,(p_2\,!)^{\pi_2}\dots}(p_1^{\pi_1} p_2^{\pi_2}\dots),$$

wherein

$$(p_1^{\pi_1} p_2^{\pi_2}\dots) = \Sigma \alpha_1^{p_1}\alpha_2^{p_1}\dots\alpha_{\pi_1}^{p_1}\,\alpha_{\pi_1+1}^{p_2}\,\alpha_{\pi_1+2}^{p_2}\dots\alpha_{\pi_1+\pi_2}^{p_2}\dots$$

$$\sum_s \pi_s p_s = n.$$

Observe that, when k is finite,

$$\Sigma\pi_s \not> k.$$

Write

$$\Sigma \frac{n\,!}{(p_1\,!)^{\pi_1}\,(p_2\,!)^{\pi_2}\dots} = C_{n,\infty},$$

but when k is finite, write $C_{n,k}$.

The relation

$$\frac{1}{\left(1-\frac{x}{1\,!}\right)\left(1-\frac{x^2}{2\,!}\right)\left(1-\frac{x^3}{3\,!}\right)\dots \textit{ad inf.}} = 1 + C_{1,\infty}\frac{x}{1\,!} + \dots + C_{n,\infty}\frac{x^n}{n\,!} + \dots$$

is seen to be true almost by intuition.

We have merely to expand the left-hand side and compare the general term with the number which $C_{n,\infty}$ denotes.

When k is finite we have

$$\frac{1}{(1-a)\left(1-a\frac{x}{1!}\right)\left(1-a\frac{x^2}{2!}\right)\left(1-a\frac{x^3}{3!}\right)\ldots\textit{ad inf.}} = \sum_{k=0}^{\infty}\sum_{n=0}^{\infty} C_{n,k}a^k\frac{x^n}{n!}.$$

This formula is consistent with the case $k=\infty$, because we have only to express the algebraic fraction as a sum of partial fractions, multiply up by $1-a$, and then put $a=1$, to reach the case of $k=\infty$. We can therefore reach it by multiplying the algebraic fraction, as it is, by $1-a$, and then putting $a=1$.

The expansion of the algebraic fraction in ascending powers of a can be made to depend upon the homogeneous product sums of the elements

$$1,\ \frac{x}{1!},\ \frac{x^2}{2!},\ \frac{x^3}{3!},\ldots.$$

Let such a product sum of degree k be denoted by

$$H_{x,k}.$$

Then
$$\sum_{n=0}^{\infty} C_{n,k}\frac{x^n}{n!} = H_{x,k}.$$

When $k=1$, we have the trivial result

$$\sum_{0}^{\infty} C_{n,1}\frac{x^n}{n!} = H_{x,1} = e^x,$$

or
$$C_{n,1} = 1.$$

A ready way of dealing with the symmetric functions of the elements

$$\frac{x^n}{n!} \qquad n = 0, 1, 2 \ldots \infty$$

is found by constructing the power-sums

$$S_{x,k} = 1^k + \left(\frac{x}{1!}\right)^k + \left(\frac{x^2}{2!}\right)^k + \ldots\textit{ ad inf.}$$

We can then, for the present purpose, employ the formula

$$H_{x,n} = \Sigma\frac{S_{x,1}^{q_1} S_{x,2}^{q_2} S_{x,3}^{q_3}\ldots}{1^{q_1}.2^{q_2}.3^{q_3}\ldots q_1!\,q_2!\,q_3!\ldots}$$

when
$$\Sigma s q_s = m.$$

It is also to be observed that if

$$A_{x,k}$$

denote the elementary symmetric function of the elements we are considering which arise in the development by multiplication of

$$(1-a)\left(1-a\frac{x}{1!}\right)\left(1-a\frac{x^2}{2!}\right)\left(1-a\frac{x^3}{3!}\right)\ldots \textit{ad inf.}$$

$$A_{x,n} = \Sigma\,(-)^{n+\Sigma q}\,\frac{S_{x,1}^{q_1}\,S_{x,2}^{q_2}\,S_{x,3}^{q_3}\ldots}{1^{q_1}\,.\,2^{q_2}\,.\,3^{q_3}\,\ldots.\,q_1!\,q_2!\,q_3!\,\ldots}$$

wherein

$$\Sigma\, sq_3 = m.$$

We next concentrate the attention upon the function $S_{x,k}$.

1.2. The case of $k = 2$, is of particular interest as it presents itself in the Theory of Probability.

We are here concerned with the sum of the *different* coefficients which arise in the binomial expansion with a positive integer exponent, viz.:

$$\begin{array}{l} 1, \\ 1+2 \\ 1+3 \\ 1+4+6 \\ 1+5+10 \\ \quad\vdots \end{array}$$

and we require a function which generates these sums of numbers. This is

$$H_{x,2} = \tfrac{1}{2}S_{x,1}{}^2 + \tfrac{1}{2}S_{x,2} = \tfrac{1}{2}e^{2x} + \tfrac{1}{2}\sum_0^\infty \left(\frac{x^n}{n!}\right)^2.$$

Since $\sum_0^\infty \left(\frac{x^n}{n!}\right)^2$ is well known to be the Bessel function

$$J_0\,(2\iota x),$$

we find that

$$H_{x,2} = \tfrac{1}{2}\,\{e^{2x} + J_0\,(2\iota x)\},$$

and by a result due to K. Neumann and Lommel*

$$H_{x,2} = \sum_0^\infty (-)^n\,\iota^n J_x\,(2\iota x),$$

which is thus seen to be an expression of the infinite series

$$1 + \frac{x}{1!} + (1+2)\frac{x^2}{2!} + (1+3)\frac{x^3}{3!} + (1+4+6)\frac{x^4}{4!} + \ldots.$$

1.3. Consider, in the next place, the associated function

$$F\,(x, y) = 1 + \frac{x}{1!} + (1+2y)\frac{x^2}{2!} + (1+3y)\frac{x^3}{3!} + (1+4y+6y^2)\frac{x^4}{4!} + \ldots,$$

which becomes $H_{x,2}$, when $y = 1$.

* 'Modern Analysis,' Whittaker and Watson, 3rd ed., p. 357.

It is easy to establish the functional equation

$$\mathrm{F}(x, y) + \mathrm{F}\left(xy, \frac{1}{y}\right) = e^{x(1+y)} + \mathrm{J}_0(2\iota xy^{\frac{1}{2}}).$$

It is a simple consequence of the way in which $\mathrm{F}(x, y)$ has been constructed.

Putting

$$xy = \omega$$

it becomes

$$\mathrm{F}\left(x, \frac{x}{\omega}\right) + \mathrm{F}\left(\omega, \frac{x}{\omega}\right) = e^{x+\omega} + \mathrm{J}_0\{2i(x\omega)^{\frac{1}{2}}\},$$

and now each side is a symmetric function of x and ω.

We deduce a particular solution

$$\mathrm{F}\left(x, \frac{x}{\omega}\right) = \tfrac{1}{2}e^{x+\omega} + \tfrac{1}{2}\mathrm{J}_0\{2i(x\omega)^{\frac{1}{2}}\},$$

and a general solution by addition of

$$\theta(x, \omega)\{\phi(x) - \phi(\omega)\},$$

where $\theta(x, w)$ is a symmetric function of x, ω; but the particular solution that is appropriate to the question before us is apparently not readily thence derivable.

However, it is easy to show that

$$\begin{aligned}
\mathrm{F}(x, y) = e^x &+ \frac{xy}{1!}\left(\frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots\right) \\
&+ \frac{x^2y^2}{2!}\left(\frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots\right) \\
&+ \dots \\
&+ \frac{x^ny^n}{n!}\left\{\frac{x^n}{n!} + \frac{x^{n+1}}{(n+1)!} + \frac{x^{n+2}}{(n+2)!} + \dots\right\} \\
&+ \dots \\
= e^x &+ \frac{xy}{1!}\int_0^x e^x\,dx + \frac{x^2y^2}{2!}\int_0^x\int_0^x e^x\,dx^2 + \frac{x^3y^3}{3!}\int_0^x\int_0^x\int_0^x e^x\,dx^3 + \dots \textit{ ad inf.} \\
= \exp &\left(xy\int_0^x dx\right) . e^x
\end{aligned}$$

symbolically.

Putting $y = 1$, we find another expression of $\mathrm{H}_{2,x}$, viz.:

$$\mathrm{H}_{2,x} = \exp\left(x\int_0^x dx\right) . e^x,$$

and thence

$$\mathrm{F}(x, y) = \left\{\exp\left(x\int_0^x dx\right)\right\}^{\nu-1} \mathrm{H}_{2,x}$$
$$= \left\{\exp\left(x\int_0^x dx\right)\right\}^{\nu-1} . \{\tfrac{1}{2}e^{2x} + \tfrac{1}{2}\mathrm{J}_0(2\iota x)\}.$$

By the transformation $xy = \omega$ as above, it will be noted that

$$\mathrm{F}\left(x, \frac{\omega}{x}\right) = \exp\left(\omega \int_0^x dx\right) . e^x$$

symbolically.

1.4. $\mathrm{A}_{x,2}$ denotes the coefficient of a^2 in

$$(1-a)\left(1-a\frac{x}{1!}\right)\left(1-a\frac{x^2}{2!}\right)\left(1-a\frac{x^3}{3!}\right)\ldots,$$

and is

$$x + \frac{x^2}{2!} + (1+3)\frac{x^3}{3!} + (1+4)\frac{x^4}{4!} + (1+5+10)\frac{x^5}{5!} + (1+6+15)\frac{x^6}{6!} + \ldots,$$

the coefficient of $x^n/n!$ being the sum of the first $\frac{1}{2}n$ or $\frac{1}{2}(n+1)$ coefficients in the expansion of

$$(1+x)^n$$

according as n is even or uneven.

In fact the infinite continued product is

$$1 - a\mathrm{A}_{x,1} + a^2\mathrm{A}_{x,2} - \ldots = 1 - ae^x + a^2\{\tfrac{1}{2}e^{2x} - \tfrac{1}{2}\mathrm{J}_0(2ix)\} - \ldots,$$

the remaining terms being expressible by means of higher transcendents as will be seen presently.

In this instance

$$\mathrm{J}_0(2ix) = 1 + \binom{2}{1}\frac{x^2}{2!} + \binom{4}{2}\frac{x^4}{4!} + \binom{6}{3}\frac{x^6}{6!} + \ldots,$$

which is seen to be equivalent to the sum of the square of the terms of the exponential series.

Moreover

$$\mathrm{S}_{x,s} = \sum_{n=0}^{\infty} \frac{(ns)!}{(n!)^s}\frac{x^{ns}}{(ns)!},$$

so that $\mathrm{S}_{x,s}$ may be looked upon as generating functions of the numbers

$$\frac{(ns)!}{(n!)^s}.$$

2. Passing to the coefficient of a^3 it appears at once that

$$\mathrm{S}_{x,3} = 1^3 + \left(\frac{x}{1!}\right)^3 + \left(\frac{x^2}{2!}\right)^3 + \ldots$$

has no simple expression in terms of Bessel Functions.

If we use the operator ϑ defined as $z(d/dz)$* the Bessel Functions of zero order satisfy the differential equation

$$(\vartheta^2 + z^2)\,y = 0,$$

* 'Theory of Bessel Functions,' Watson, Cambridge, 1922, page 19.

and we have found the relation

$$S_{x,2} = J_0(2\iota x).$$

By analogy we are led to construct the differential equation of the third order

$$\{\vartheta^3 + (\tfrac{3}{2}z)^3\} y = 0,$$

of which a solution is

$$1 - \frac{z^3}{2^3(1!)^3} + \frac{z^6}{2^6(2!)^3} - \frac{z^9}{2^9(3!)^3} + \dots .$$

If herein we put

$$z = 2\rho_3 x$$

where

$$\rho_3^3 + 1 = 0$$

and ρ_3 is a primitive root of negative unity, we obtain

$$S_{x,3}.$$

2.1. We now observe that the Bessel Functions, of order n, satisfy the differential equation

$$\{(\vartheta - n)(\vartheta + n) + z^2\} y = 0,$$

and we are led to the construction of the differential equation of the third order

$$\{(\vartheta - n)^2 (\vartheta + 2n) + (\tfrac{3}{2}z)^3\} y = 0,$$

and thence to one of its solutions

$$\sum_{r=0}^{\infty} \frac{(-)^r z^{n+3r}}{2^{n+3r}(r!)^2 (n+r)!}.$$

2.11. From this point it is easy to construct the differential equation of order m

$$\{(\vartheta - n)^{m-1}\{\vartheta + (m-1)n\} + (\tfrac{1}{2}mz)^m\} y = 0,$$

and to establish, by the method set forth by Watson, *loc. cit.*, page 39, a solution

$$E_{n,m}(z) = \sum_{r=0}^{\infty} \frac{(-)^r z^{n+rm}}{2^{n+rm}(r!)^{m-1}(n+r)!},$$

a transcendent which involves two orders n, m; a first order n and a second order m.

If

$$\rho_m^m + 1 = 0,$$

ρ_m a primitive m^{th} root of unity,

$$E_{0,m}(2\rho_m x) = S_{x,m} = 1^m + \left(\frac{x}{1!}\right)^m + \left(\frac{x^2}{2!}\right)^m + \left(\frac{x^3}{3!}\right)^m + \dots .$$

In terms of these transcendents we can express, by the formulæ given in 1.1 both

$$H_{x,n} \text{ and } A_{x,n}.$$

2.2. The transcendents enjoy properties analogous to those of the Bessel Functions.

The general differential equation may be regarded as valid when m is an integer > 1.

We have
$$(\vartheta - n) \mathrm{E}_{n,0}(z) = 0$$
$$\left(\frac{d}{dz}\right)^n \left(\frac{d}{dz} + \frac{1}{2}\right) \mathrm{E}_{n,1}(z) = 0.$$

2.21. A second solution of the general differential equation is
$$\mathrm{E}_{-(m-1)n,m}(z) = \Sigma \frac{(-)^r (\frac{1}{2}z)^{-(m-1)n+rm}}{r!\,\{\Gamma(-n+r+1)\}^{m-1}},$$
and it appears that the two fundamental solutions are valid for any complex value of m.

2.22. A leading result in the Theory of Bessel Functions is
$$\exp \tfrac{1}{2}z(t - t^{-1}) = \sum_{-\infty}^{\infty} \mathrm{J}_n(z)\, t^n.$$

In analogy we can establish the formula
$$\mathrm{E}_{0,1}(-zt)\, \mathrm{E}_{0,m-1}(zt^{-1/m-1}) = \sum_{n=-\infty}^{\infty} \mathrm{E}_{n,m}(z) t^n.$$

The left-hand side is
$$\sum_{r=0}^{\infty} \frac{z^r t^r}{2^r \,.\, r!} \sum_{s=0}^{\infty} \frac{(-)^s z^{s(m-1)} t^{-s}}{2^{s(m-1)} (s!)^{m-1}}.$$

In order to find the coefficient of t^n we make $r = n + s$ for a fixed value of s, and obtain
$$\Sigma \frac{(-)^s z^{n+sm}}{2^{n+sm} (s!)^{m-1} (n+s)!} t^n = \sum_{n=-\infty}^{\infty} \mathrm{E}_{n,m}(z)\, t^n$$
establishing the result.

For $m = 2$ it will be noted that
$$\mathrm{E}_{0,1}(-zt) = e^{\frac{1}{2}zt}; \ \mathrm{E}_{0,1}(zt^{-1}) = e^{-\frac{1}{2}zt^{-1}}.$$

2.23 If $m \neq 1$, we can put $zt^{-(m-2)2/m-2}$ for z, and obtain
$$\mathrm{E}_{0,1}(-zt^{m/2m-2})\, \mathrm{E}_{0,m-1}(zt^{-m/2m-2}) = \sum_{n=-\infty}^{\infty} \mathrm{E}_{n,m}(zt^{-(m-2)2/m-2}) \,.\, t^n.$$

If we put $m = 0$, we eliminate t, obtaining
$$\mathrm{E}_{0,1}(-z)\, \mathrm{E}_{0,1}(z) = \sum_{n=-\infty}^{\infty} \mathrm{E}_{n,0}(z).$$

2.24. Consider the expansion, by Laurent's Theorem, of
$$\mathrm{E}_{0,1}(-zt)\, \mathrm{E}_{0,m-1}(zt^{-1/m-1})$$
in a series of positive and negative powers of t.

We have

$$\mathrm{E}_{n,m}(z) = \frac{1}{2\pi\iota}\int^{(0+)} u^{-n-1}\,\mathrm{E}_{0,1}(-zu)\,\mathrm{E}_{0,m-1}(zu^{-1/m-1})\,du.$$

To express $\mathrm{E}_{n,m}(z)$ in a power series in z, write $u = 2t/z$; then

$$\mathrm{E}_{n,m}(z) = \frac{1}{2\pi\iota}\int^{(0+)} \left(\frac{z}{2t}\right)^{n+1} e^t\,\Sigma\,\frac{(-)^s\,(zu^{-1/m-1})^{s(m-1)}}{2^{s(m-1)}\,(s\,!)^{m-1}}\,\frac{2}{z}\,dt$$

$$= \frac{1}{2\pi\iota}\int^{(0+)} \left(\frac{z}{2t}\right)^{n+1} e^t\,\Sigma\,\frac{(-)^s\,z^{s(m-1)}\left(\dfrac{2t}{z}\right)^{-s}\dfrac{2}{z}\,dt}{2^{s(m-1)}\,(s\,!)^{m-1}}$$

$$= \frac{1}{2\pi\iota}\int^{(0+)} \left(\frac{z}{2t}\right)^{n+1} e^t\,\Sigma\,\frac{(-)^s\,z^{sm-1}\,t^{-s}\,dt}{2^{sm-1}\,(s\,!)^{m-1}}$$

$$= \frac{1}{2\pi\iota}\int^{(0+)} \Sigma\,\frac{(-)^s\,z^{n+sm}\,t^{-n-1-s}\,e^t\,dt}{2^{n+sm}\,(s!)^{m-1}}.$$

Now the residue of the integrand at $t = 0$ is $\{(n+s)!\}^{-1}$; so that, if n is a positive integer or zero,

$$\mathrm{E}_{n,m}(z) = \sum_{s=0}^{\infty} \frac{(-)^s\,z^{n+sm}}{2^{n+sm}\,(s!)^{m-1}\,(n+s)\,!},$$

a verification.

2.25. It is convenient to write the first and second solutions of the differential equation

$$\mathrm{E}_{n,m}(z)\,;\ \mathrm{E}_{[n,m]}(z)$$

so that

$$\mathrm{E}_{[n,m]}(z) = \mathrm{E}_{-(m-1)n,m}(z)\,;$$

then it is easy to shew that

$$\frac{d}{dz} z^{(m-1)n}\,\mathrm{E}_{(n,m)}(z) = \tfrac{1}{2}mz^{(m-1)n}\,\mathrm{E}_{(n-1,m)}(z) \tag{A}$$

leading to the recurrence formula

$$(m-1)\,n\mathrm{E}_{(n,m)}(z) + z\mathrm{E}'_{(n,m)}(z) = \tfrac{1}{2}mz\mathrm{E}_{(n-1,m)}(z).$$

Also

$$\frac{d}{dz}\left(z\frac{d}{dz}\right)^{m-2} z^{-n}\mathrm{E}_{[n,m]}(z) = (\tfrac{1}{2}m)^{m-1} z^{m-n-2}\mathrm{E}_{[n+1,m]}(z) \tag{B}$$

The formula (A) may be written

$$z^{-(m-1)n}\frac{d}{dz} z^{(m-1)n}\,\mathrm{E}_{(n,m)}(z) = \tfrac{1}{2}m\mathrm{E}_{(n-1,m)}(z)\,;$$

or, say,

$$\mathrm{V}_n\mathrm{E}_{(n,m)}(z) = \tfrac{1}{2}m\mathrm{E}_{(n-1,m)}(z).$$

So that

$$\mathrm{V}_{n-r+1}\mathrm{V}_{n-r+2}\ldots\mathrm{V}_n\mathrm{E}_{(n,m)}(z) = (\tfrac{1}{2}m)^r\,\mathrm{E}_{(n-r,m)}(z) \tag{C}$$

Formula (B) may be written

$$z^{-m+1}\frac{d}{dz}\left(z\frac{d}{dz}\right)^{m-2} z^{-n}\mathrm{E}_{[n,m]}(z) = (\tfrac{1}{2}m)^{m-1} z^{-n-1}\mathrm{E}_{[n+1,m]}(z);$$

so that writing $\quad \mathrm{W}_n\, z^{-n}\mathrm{E}_{[n,m]}(z) = (\tfrac{1}{2}m)^{m-1} z^{-n-1}\mathrm{E}_{[n+1,m]}(z)$

$$\mathrm{W}_{n+r-1}\mathrm{W}_{n+r-2}\ldots\mathrm{W}_n\, z^{n}\mathrm{E}_{[n,m]}(z) = (\tfrac{1}{2}m)^{(r-1)(m-1)} z^{-n-r}\mathrm{E}_{[n+r,m]}(z), \qquad \text{(D)}$$

reducing to known Bessel Function formulæ when $m = 2$.

A Universal Interferometer.

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(Received April 26, 1923.)

(Plates 13 and 14.)

In a communication to the Royal Society in the year 1909* the author described, by the kind authorisation of the Board of Trade, an Interferential Comparator for Standards of Length, which had been provided, under his direction and at the request of the Board, for the Standards Department. The essential novelty presented by the comparator was that each of the two travelling microscopes, employed to observe and read the positions of the two fiducial marks forming the limits of the standard bar, the imperial yard for instance, was given so exceedingly fine and steady a movement that the truly plane and polished surface of a black glass disc carried by the microscope could form one of the two reflecting surfaces producing the interference bands. The movement of the microscope parallel to itself and to the length of the bar, over a very true V-and-plane guiding bed, was thus accompanied by movement of the interference bands parallel to themselves and to the vertical pair of spider-lines of the autocollimating telescope, which was used, along with a constant deviation prism and a hydrogen, cadmium, or neon Geissler vacuum tube, for the production and observation of the bands in light of a single specific wave-length.

The success of this apparatus, owing to the steadiness and perfect control of the movement of the magnificent field of interference bands afforded—in red hydrogen or cadmium, or yellow neon light—suggested the suitability of employ-

* 'Phil. Trans.,' A, vol. 210, p. 1 (1910).—Comparator paper.

ing such a microscope, together with the optical train and an adequate length of the V-and-plane bed, as an interferometer of the most perfect character and of completely general application, for the measurement of small amounts of

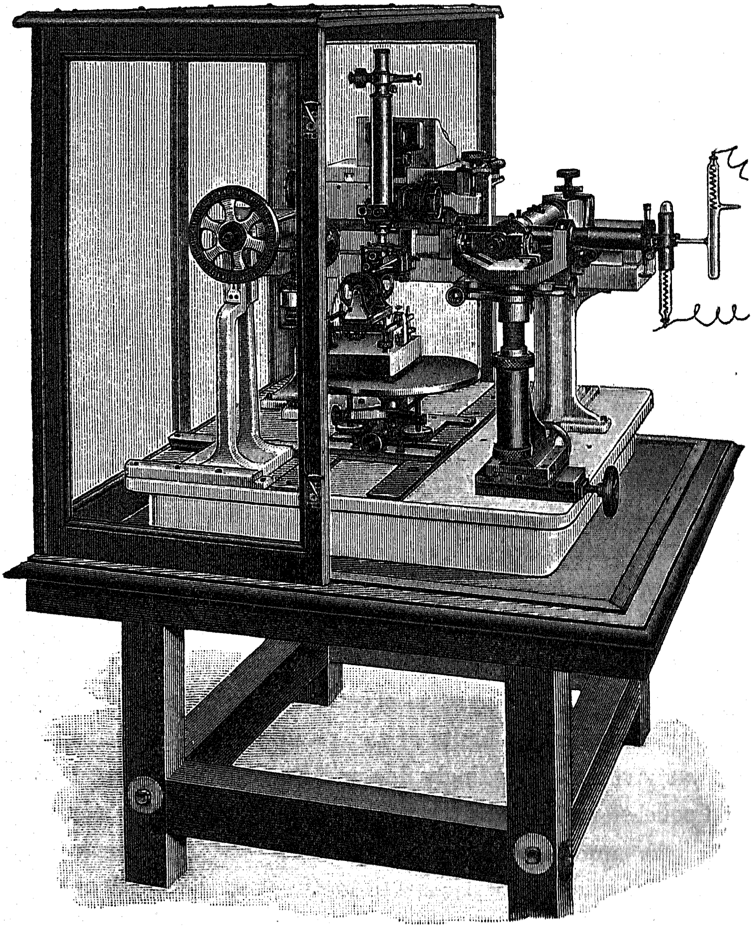

Fig. 1.—The Universal Interferometer with Torsometer.

motion, slight deformations, short distances, or minute objects, of any nature whatsoever.

Such an apparatus has therefore been constructed for the author by Messrs. Troughton and Simms, whose experience in the construction of the standard comparator and of the elasmometer, the interferential elasticity apparatus described by the author† in 1903, has proved invaluable. Messrs. R. and J. Beck have collaborated as regards the microscope, and Messrs. Hilger as regards

† 'Phil. Trans.,' A, vol. 202, p. 143 (1904).—Elasmometer paper.

the constant deviation prism and the truly plane-surfaced glass plates. It includes also a universally adjustable work-table for the support and adjustment of any object, or instrument carrying the object and causing its motion, which it is desired to measure or the movement or deformation of which is to be measured.

A general view of the whole apparatus, in its air-tight glass case on a strong stand and with the torsometer described in the next communication in position on the adjusting table, is given in fig. 1; and the universal interferometer is shown alone in fig. 2 (Plate 13). The glass case is a very essential part of the apparatus, as it is imperative to protect the delicate screw and guides from dust particles, and the iron and steel portions, which are kept well oiled, from damp. The woodwork is well seasoned Spanish mahogany, and the case is constructed in two halves (one of which is removed in the figure), separately detachable, and locked together when in position by four nickel-plated binding hooks.

Two further illustrations, side views from the left and right ends of the instrument respectively, are also given in figs. 3 and 4 (Plates 14 and 13), which will assist in elucidating the details in a manner impossible from the front.

The interferometer consists of eight main parts, as numbered consecutively in the following description, the whole being mounted on a very rigid cast-iron base, resting in turn on the mahogany table-plinth of the case and stand.

(1) *The V-and-Plane Guiding Bed* is very stoutly constructed of specially chosen cast-iron. It is 30 inches long, and lies freely, unbolted, in a plinth of the same metal, which is supported parallel to the base, at a convenient height above the latter, by two bracket-pillars to which it is securely bolted. These pillars are arranged at the Airy positions for no flexure of the plinth and guiding bed, and specially shaped, with backward extension, to ensure rigidity. A large free space is thus left under the arch, between the pillars, for the accommodation of the work-table and whatever object or instrument it is to carry. The sectional shape of the bed and plinth, and the shape of the supporting bracket-pillars, will be clearest from fig. 3, Plate 14.

Very special care was taken with the true-planing of the V and the plane, as any irregularity would cause distortion of the interference bands, or at least an alteration of their width and twisting out of their upright position.

The front face of the bed is grooved above and below to form a projecting dove-tail, in order to afford sliding support and fixation at the desired positions for the three fittings carrying respectively the constant deviation prism, the interference glass plates, and the Grayson-ruling fiducial marks. The broad face of the dove-tail is divided as a millimetre scale along its whole length.

(2) *The Microscope* is mounted vertically by a rigid bracket, counterpoised behind in an adjustable manner, and also adjustable for its overhang in front of the V-and-plane bed, on a thick slab of the same cast-iron as the bed. This slab slides, with V-and-plane contact as shown best in fig. 4, Plate 13, over a thicker block of steel, the movement being effected by the fine screw which is the all important feature of the whole apparatus. The thick block slides similarly by V-and-plane contact over the main guiding bed by hand, thereby affording the rough adjustment of the position of the microscope ; it can be fixed at the desired position by means of a locking lever working from behind. All these further V's and planes have been most carefully truly planed. The construction of the blocks and of the fine screw of one-fiftieth inch (half-millimetre) pitch, with its large silver drum-head divided directly into a thousand parts, outer milled head, and worm wheel of 100 teeth driven by an endless screw, are practically as described on pages 17 to 19 of the comparator memoir.* The endless screw can be thrown out of gear when not in use, by lowering a lever handle, and it springs automatically into gear when the lever is again raised.

The only difference in construction is that the weight-relieving device is even more perfect, the four spring pistons which take off the greater part of the weight of the microscope and its carrier slab (thereby leaving less work for the fine screw to do) terminate now in steel ball-bearing rollers of $1\frac{3}{8}$-inch diameter, no less than nine-tenths of the total weight to be driven by the screw being now eliminated, instead of only two-thirds as in the case of the comparator. A scale of fiftieths of an inch, the pitch of the screw, directly divided on silver is carried on the front of the block, and an indicator for it on the microscope-carrying slab. This enables the number of complete revolutions of the screw to be recorded, and with the divided drum affords the means of ordinary mechanical measurement to the fifty-thousandth of an inch.

The microscope is mounted centrally on the sliding block. The drum and driving end of the screw is placed to the left. The microscope carries the black glass interference disc, of $1\frac{3}{8}$-inch diameter, on the right side ; but it is not attached to the tube of the microscope but to its rigid carrying bracket, so that it is quite unaffected by the focussing movement of the microscope and alterations for height of the latter. Another difference, moreover, concerns the mode of illuminating the Grayson rulings or other fiducial marks or opaque objects under observation. A pointolite lamp, adjustably mounted, as supplied by Messrs. Beck, is used as the source of light ; it is placed in front of the instrument but at some distance away, behind and slightly to the left of the observer. Parallel or slightly converging rays are produced by a con-

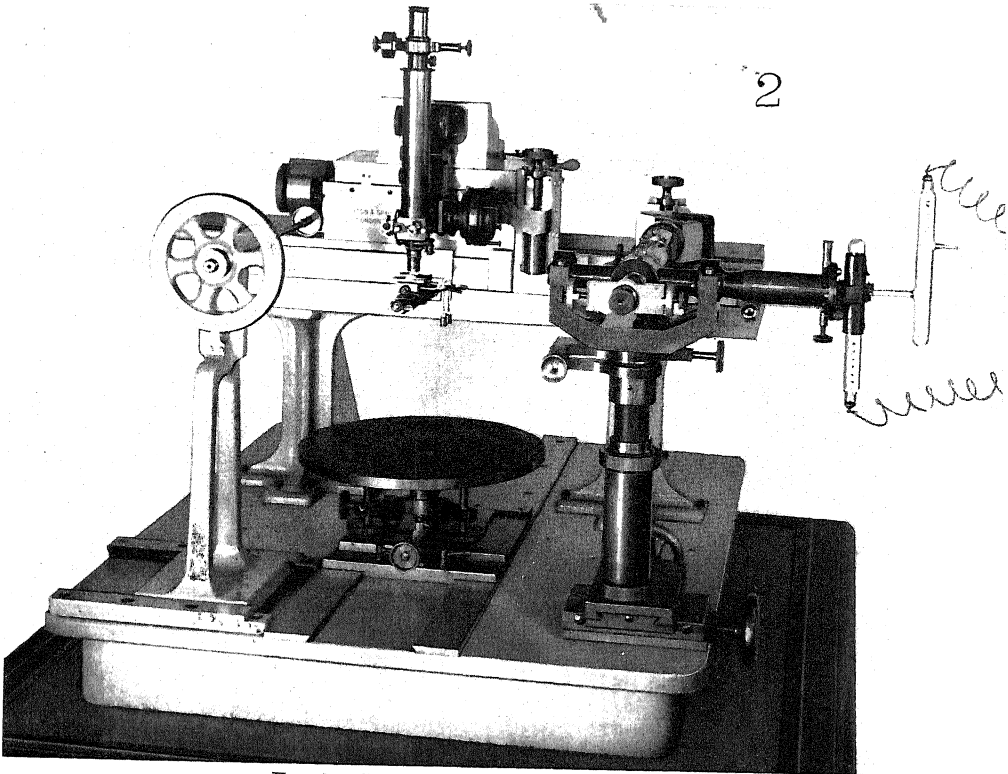

FIG. 2.—The Universal Interferometer alone.

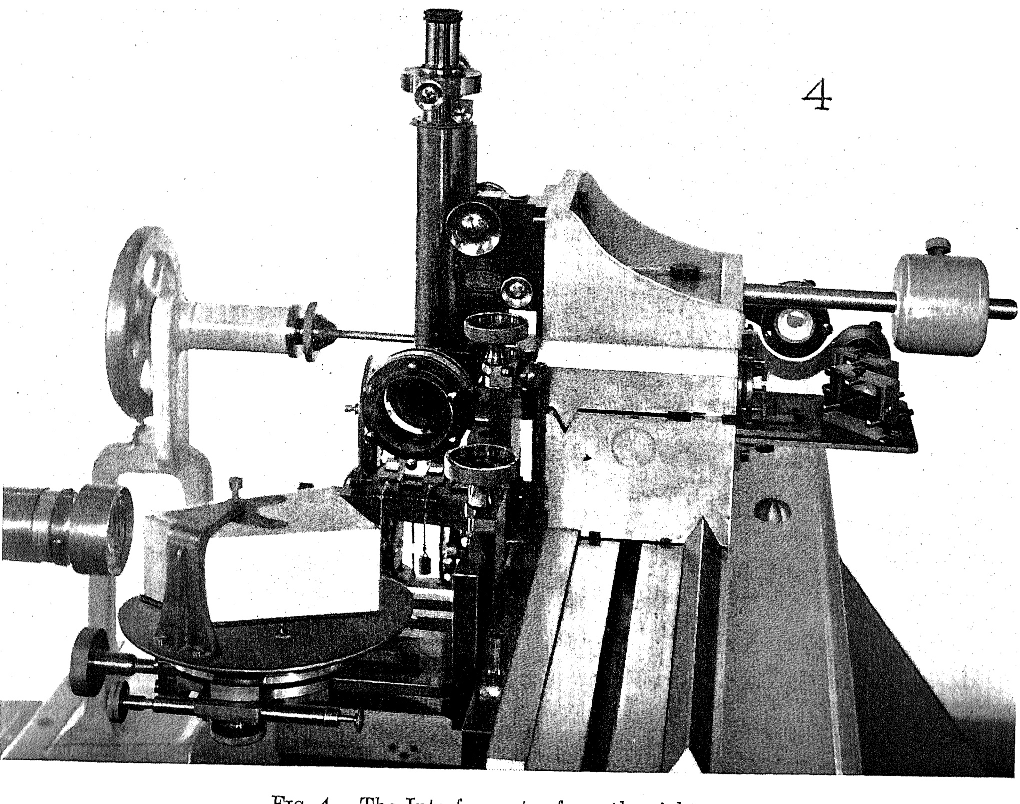

FIG. 4.—The Interferometer from the right.

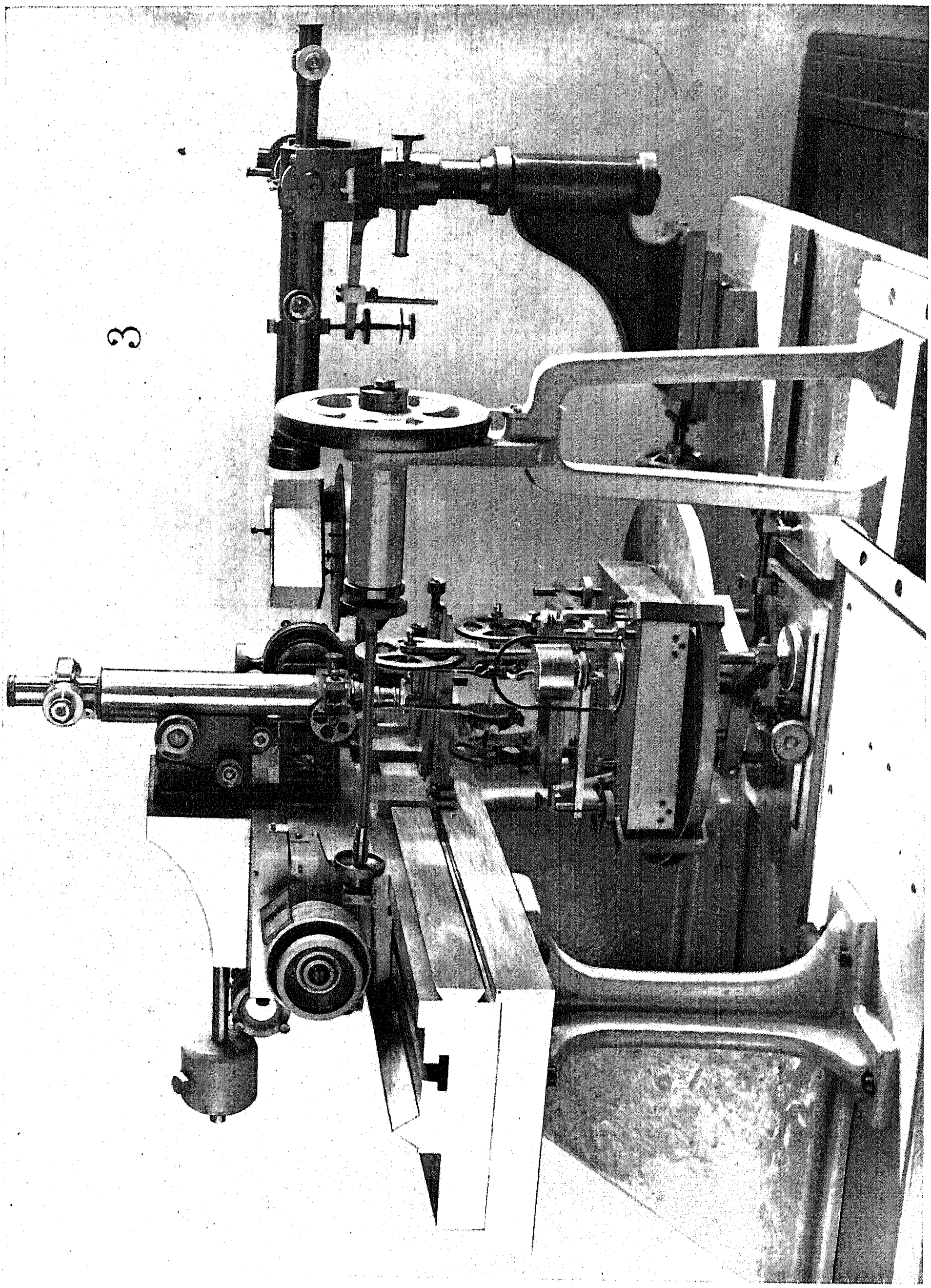

Fig. 3.—The Interferometer and Torsometer from the left.

densing lens combination, forming a front fitting to the pointolite lamp and having a signal green glass screen mounted in front of it, in order to get the best resolution of the Grayson rulings; the rays are directed on to a small totally reflecting prism carried at the left side of the microscope, opposite an aperture in the lower box-like part of the microscope body-tube which contains the adjustable glass-plate reflector for the illumination of opaque objects. A diaphragm wheel, pierced with five circular apertures of graduated diameters, is mounted alongside, so that by adjustment of prism, wheel and reflector, the maximum illumination and most suitable lighting for the sharpest resolution of the rulings or other fiducial mark or object can be attained.

For the observance of Grayson ruling fiducial marks, consisting of five parallel lines one forty-thousandth of an inch apart, a specially constructed $\frac{1}{15}$-inch dry objective was employed on the comparator. Mr. Conrad Beck has given special consideration to this problem, and carried out a prolonged experimental investigation, with the result that it is now possible to obtain an equally good magnification (nearly 3,000 diameters) and superior resolution of the rulings, which appear as if about a millimetre apart, by the use of a Beck $\frac{1}{6}$-inch (4 mm.) apochromatic objective, with a specially high eyepiece (focal length 5 mm.) magnifying 50 times. The better resolution is due to the higher numerical aperture, 0.95, of the $\frac{1}{6}$th, as compared with the 0.8 N.A. of the dry $\frac{1}{15}$th. There is also better definition, owing to the new objective being apochromatic. Further, a very important advantage is gained, that of a greater working distance, a considerably thicker film of air, very clearly visible, intervening between the objective and the cover-glass of the Grayson rulings, which are exceedingly fine diamond scratches, on plates of speculum metal a centimetre square and two millimetres thick. Besides a very rigid coarse movement with locking screw-clamp, two fine movement screws are provided, one twice as fine as the other, one on each side of the bracket, the finer one being graduated in hundredths of a millimetre for measuring thickness.

The low power provided is a $\frac{2}{3}$-inch (16 mm.) object glass of N.A. 0.13 and with specially long working distance. Two eyepieces are available for use with it, magnifying eight and 15 times respectively, their focal lengths being 30 and 10 mm. Using these two eyepieces the magnification afforded by this low power is about 150 and 282 times respectively.

The high power objective is provided with a collar correction for using cover-glasses of different thickness. The ordinary cover-glasses are about 0.006 inch thick, but this is raised to 0.009 inch of equivalent glass by the cementing medium used with the cover-glasses of the Grayson rulings. The correct setting

of the objective for this thickness of cover glass is to the 22 position (22/100 graduation).

(3) *The Driving Wheel,* the large graduated wheel seen on the left front of the instrument, is divided into degrees, and connects with the endless screw which drives the fine movement screw by a flexible-coil steel shaft. This flexible shaft, which altogether prevents any binding anywhere, is a great success, and it is possible to drive the microscope so steadily and accurately by means of it that the interference bands, which move simultaneously with the microscope, may be brought to rest at any position within a tenth of a band with the greatest ease. The wheel is mounted in rigid bearings carried at the summit of a double pedestal, which springs from a base capable of sliding adjustment and eventual rigid fixation in guides. This arrangement of the driving wheel on the extreme left, together with that of the interferometer telescope on the extreme right, leaves the whole middle front clear for work with any apparatus which may be mounted on the large central adjusting table. A complete revolution of the wheel corresponds to the movement of the microscope for one five-thousandth of an inch, or one two-hundredth of a millimetre (0.005 mm.), and it causes 15 interference bands in red hydrogen light to pass the reference centre. Thus about 24° of rotation of the wheel corresponds to the passage of each band.

(4) *The Interferometer autocollimating Telescope,* with micrometer eyepiece, and Geissler tube attachment at the end of the side tube, is precisely as described in the memoirs on the comparator* and elasmometer†, except that the lower part of the pedestal support is carried forward on a bracket (best shown in fig. 3) which springs from the upper of the two centering movements.

(5) *The Constant Deviation Prism* is one of the largest size constructed by Hilger, with truly planely worked surfaces and of refractive index 1.651 for sodium light. It is mounted on a rotating table, with silver divided circle, carried by a fitting which slides along the dove-tail of the V-and-plane bed, and which is fixed at the correct position opposite the telescope by means of a strong clamping screw with lever handle. It is provided with adjustments by milled-headed closely fitting screws for height, and for its position backwards and forwards perpendicular to the V-and-plane bed.

(6) *The Glass Interference Discs* are arranged on an adjustable fitting also carried on the dove-tail, along which it is capable of sliding to the convenient place and fixation there by another clamping screw with lever head. It is shown in elevation in fig. 5, from which the situation of the two colourless glass circular plates, g_1 and g_2, or more accurately wedges, with respect to each

other and to the black glass disc g_3, carried by the microscope, will best be appreciated. They are 5 cm. in diameter and a centimetre thick, and all four

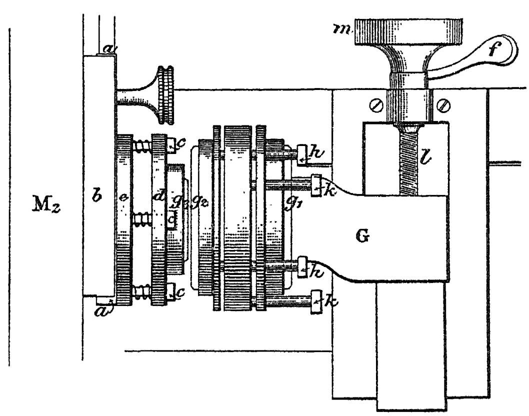

FIG. 5.—The Glass Interferometer Discs and their Adjustments.

surfaces are worked truly plane by Hilger. The two surfaces of any one and the same disc are slightly inclined exactly to the same extent, 35′, out of strict parallelism to each other, indeed the two plates were cut from one wedge of glass of this angle. The essential surface, relevant to the production of the interference bands, is that surface of g_2 which is adjacent to, and separated usually by about three-fourths of a millimetre from, the polished surface of the black glass disc g_3 carried by the microscope. The other surface of this black glass plate is matt and covered with absorbent lamp-black paint, so can be neglected. The tilt of 35′ is given to the second colourless glass surface of g_2 in order to eliminate its reflection out of the field of view of the telescope, being thrown behind and intercepted by the iris diaphragm of the latter. As this tilt, however, introduces a little refraction, this latter is corrected by introducing the duplicate wedge g_1, which is arranged for the purpose contrariwise, the thicker part of the one disc being opposite to the thinner part of the other, and the imaginary edge of the wedge being horizontal in each case. The two reflections from g_1 are got rid of by minute rotation of this corrective disc (about half a degree) about a vertical axis. The reflections from five truly plane glass surfaces have thus to be dealt with, and the two proper ones required (from the surfaces forming the air film) have to be carefully isolated. When the discs are properly adjusted, by means of the little screws h and k, the images of the rectangular signal-stop (at the common focus of the objective and eyepiece of the telescope) from the two essential surfaces

overlap each other almost completely, being vertically identical but horizontally to a slight extent not quite completely overlapping, while the reflections from the other three unessential surfaces occupy echelonned positions in the telescope field when the iris diaphragm is fully open, but are cut off when it is partially closed, the pair of overlapping images then occupying centrally and alone the greater part of the field. During this operation white light is used, and the telescope has its simple eyepiece in front, which makes it an ordinary telescope for parallel rays. When this eyepiece is replaced by the special micrometer eyepiece, the telescope focusses the essential surface of the colourless glass disc g_2, which bears at its centre a little silvered ring enabling the focussing to be exact and acting as the centre of reference for the interference bands. When the white light is replaced by the monochromatic light for which the prism is adjusted, say red hydrogen light, the vacuum tube in use being one of which the residual gas is hydrogen, the field is covered with about a dozen parallel vertically arranged dark interference bands, on the red ground of light corresponding to the red line C of hydrogen. The silver ring is also clearly focussed still, as well as the pair of vertical spider-lines and single horizontal line of the Ramsden micrometer. The conversion of the telescope for infinity into one focussing the bands (which are localised in the neighbourhood of the air-film) is effected by an additional lens carried in the eyepiece tube between the Ramsden ocular and the signal stop; this latter is situated closely in front of the little totally reflecting prism which half covers the circular aperture at the focus of the objective, at the junction of the main tube with the side tube. For the rays from the Geissler tube (or the white light lamp during the adjustment of images) are received on the other rectangular surface of this little right-angled prism and reflected by the 45° hypotenuse through the surface diaphragmed by the stop, which latter thus acts as the light source; the rays then pass to the objective, and thence to the constant deviation prism and to the interference discs, and return after reflection from the two essential glass surfaces along almost exactly the same path, the ideal condition for sharp interference, coming to the observer's eye through the other open half of the little circular aperture (almost touching the stop-source), the additional lens and the eyepiece.

(7) *The Grayson-Rulings Fiducial Mark Fitting* is the third and last of the sliders along the dove-tail front face of the V-and-plane bed. It is clamped at a position which brings the rulings conveniently under the microscope. Essentially it consists of the support and adjustments for a little counterpoised slider, moving parallel to the movement of the microscope by the least applica-

tion of a push, and which carries the Grayson ruling fiducial mark or signal already described. Prof. Grayson prepared a number ruled on different materials, for the author and for the Standards Department, but the most useful and cleanest ruled are those made on speculum metal and covered with a cover-glass as already mentioned. For most purposes one such signal on a single slider will suffice, but for use with the torsometer, to be described in the next paper, two are desirable, parallel to each other.

Hence, this fitting comprises two small sliders of gunmetal, sliding with V-and-plane contact, on brass V-and-plane guides, each slider being counterpoised by a weight (small shot) contained in a little cylindrical cup, suspended by a silken cord which passes over a pulley. The slider, with its ruling on a plate of polished speculum metal one centimetre square and two millimetres thick, cemented on it by a thin film of balsam in benzene, thus moves in each case at the slightest touch. The guides of the two sliders are mounted on a dove-tailed bed, provided with long driving screw, gearing with one of them in order that the distance apart of the two sliders can be varied and adjusted to that which is most convenient for the work in hand. In addition, this whole guiding bed is mounted on a lower one, also provided with a long screw, which enables both sliders to be moved simultaneously, by means of the lower milled head, also perpendicularly to the sliders and their direction of motion.

The actual appearance of one of these Grayson signals or fiducial marks under the microscope, using the $\frac{1}{6}$th power objective and the special high power eyepiece, is shown in fig. 6. Besides the five lines ruled 1/40,000th-inch apart,

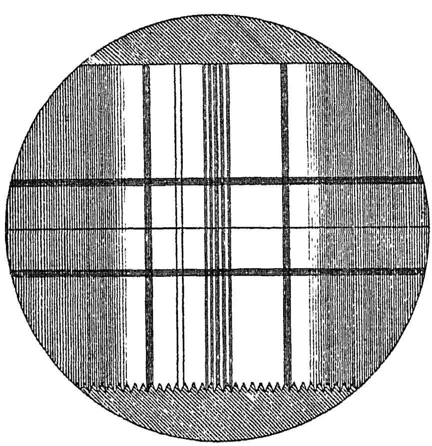

FIG. 6.—The Grayson Ruling Signal.

there are also four thicker finder-lines in view, and also the pair of vertical spider-lines and the single horizontal line of the micrometer.

(8) *The Adjustable Work-Table*, the round table seen in the centre of the instrument, is a stout truly planed bronze plate, strengthened beneath with radiating ribs, intended for the support of the work in hand for measurement. This work may take the form of the object itself which is to be measured, or to have its movement or change of dimensions measured under the application of some force or other agency; or it may be an instrument, the torsometer described in the next communication for instance, on which the object is mounted, and which is causing its movement or alteration of shape and dimensions.

The table has four essential means of adjustment: (*a*) Its height can be varied by two inches by means of the three levelling screws, which stand in carefully adjusted toe plates screwed down to the rectangular base-plate on which the table is mounted. (*b*) This base-plate is capable of sliding in steel guides running across the whole length front-and-back, parallel to the two sides of the main heavy base of the instrument. This enables the position of the work-table to be varied forwards or backwards, in or out of the arch-recess. When the position has been roughly adjusted by hand, a locking strip of the base-plate in front is clamped to the main base by means of two lever-handled locking screws. (*c*) The position can then be finely adjusted for front-to-back movement and side-to-side movement, by two rectangularly arranged fine movement screws, the former affording three inches of fine adjustment and the latter two inches. For the purpose of this latter side-to-side movement the rectangular base-plate is made double, the upper portion being the side-to-side slider, and the lower carrying its bevelled guides. These movements occur with some stiffness, so that the work-table is very rigid when at rest. (*d*) It can also be rotated in its own plane by means of a strong tangent screw, hidden in the figures as it is situated behind. In order to supply the means of raising a small object close up to the microscope, a specially rigid tripod to stand on the work-table, with long screws affording a very considerable amount of adjustment for height and a truly plane table top, is also furnished. Some convenient clamps and binding screws are also provided, for securing the work on the work-table or tripod-top, and the latter to the work-table.

There are also provided, at the back of the instrument, shown only in figs. 3 and 4 (Plates 13 and 14), the two circular mirrors and two inclined glass plates of a Michelson interferometer, and also the two circular plates of a Fabry and Perot étalon. All the circular plates are silvered, and one of the rectangular ones, on one surface in each case, as is usual in the Michelson and the Fabry

and Perot interferometers. In each case the movable mirror or plate is carried rigidly by the iron slab which carries the microscope, so that they move with the latter, while the others are fixed to fittings carried by the thick steel block over which the slab moves. All the plates are mounted in frames, provided with the means of delicate adjustment of the plates to the positions required for the production of the interference fringes. Hence it is possible, if the observer prefers or considers it desirable, to use the interferometric method of Michelson or that of Fabry and Perot, instead of that of the author, for the measurement of the movement of the microscope.

Consequently this instrument provides the means of employing all the best methods of measurement by means of wave-lengths of light, as well as the most delicate mode of measurement by mechanical means. It can, therefore, be truthfully said to be a universal interferometer and an instrument for the finest modes of measurement (excluding the use of X-rays) yet known to us.

Adjustment of the Instrument.—The interferometer only requires to be adjusted once for all, except for the last touches to be given each time it is used, assuming the instrument to be set up in a permanent position, on as solid a floor as possible. The first operation is to set the thick circular black glass disc g_3, carried by the microscope bracket closely alongside and moving rigidly with the microscope itself, so that its polished truly plane surface is exactly vertical and perpendicular to the direction of movement of the microscope when actuated by the all important fine traversing screw. The two larger colourless glass discs g_2 and g_1 of the interference apparatus, arranged approximately parallel to each other, in their fitting, are brought into the required position by the sliding of the fitting along the dove-tail face of the V-and-plane bed, until the outer (nearest the microscope) surface of g_2 is within a millimetre of and parallel to the black glass surface, and so that the three glass discs have their centres on a common axis which is perpendicular to the black glass and parallel to the main V-and-plane bed. The autocollimating telescope, illuminated by a white light lamp with clouded globe, is also brought into position, with the telescope axis horizontal and directed normally at the V-and-plane bed, at the height of the axis of the glass plates just referred to. The constant deviation prism-table on its adjustable fitting is also slid along the dove-tail face of the V-and-plane bed to its correct position opposite to the telescope, but that prism is not at first mounted on it, but instead a large totally reflecting prism (the one constructed for the author's interference dilatometer and used also in adjusting the elasmometer being specially suitable, as it has all needful means of adjustment provided with it) is laid on the centre of the rotatable table, that centre

being at the junction of the telescope axis and the axis of the interference discs, these two axes making a right angle with each other in the horizontal plane.

The images of the little rectangular stop forming the exit face (or more correctly masking that face, the mask-stop having a rectangular aperture) of the small totally reflecting autocollimating prism, at the common focus of the objective and the simple eyepiece (the latter being in position and not the micrometer eyepiece), reflected by the five glass surfaces of the interference discs are then to be obtained and adjusted to their proper positions with the aid of the large totally reflecting prism. Only the two colourless glass discs are to be moved, the black glass disc g_3 being left precisely as already adjusted; the two colourless discs are to be adjusted with respect to it. The image from the black glass surface is first brought near the centre of the field, in the illuminated semicircular half of the field as seen by the common eyepiece, and close to the vertical dividing line between that and the dark half (covered by the little autocollimating prism), by use of the big reflecting prism. The four other rectangular images of the stop are then brought into the field, if not already there, and adjusted to their correct positions by manipulation of the adjusting screws of the two colourless glass discs, three blackened screws adjusting g_2 and three bright lacquered screws adjusting g_1. The process is fully described, and illustrated in fig. 904, on page 1355 of Vol. II of the 1922 edition of the author's "Crystallography and Practical Crystal Measurement."

The image from the g_2 surface nearest to the black glass is correctly placed when it is brought to cover that from the latter completely vertically and nearly but not quite completely horizontally, the two glass surfaces being then very slightly inclined to each other, the air-film being not strictly a parallel-surfaced one but minutely wedge-shaped, the edge of the wedge being vertical, the condition for upright, parallel, rectilinear bands. These two images are then isolated and the other three images arranged *en echelon* at the corners of a rhombus and screened off by the partial closure of the iris diaphragm.

The large totally reflecting prism is then replaced by the constant deviation prism, arranged on the rotating circle in the correct position for constant deviation, as fully described in the author's "Crystallography," Vol. II, pages 967 and 968. The four images of the stop-source of light (the important one double), in white light, will then be replaced by four correspondingly arranged horizontal continuous spectra. The white light lamp is then removed from the collimating side tube, and replaced by the vacuum tube in its adjustable fitting, which slides on the end of the side tube. The hydrogen vacuum tube should be used in these adjustments, as most convenient, when the continuous spec-

trum in each case, while still faintly persisting, will be replaced by brilliant images of the rectangular stop in red light, if the constant deviation prism is somewhere about the proper position for use of the red C-light, and if not, a slight rotation of the prism circle by the tangent screw will be adequate so to adjust it, the correct position being when the full rectangle is filled with the brilliant red light. The simple eyepiece is now replaced by the micrometer eyepiece, with the additional lens in position, which changes the telescope for parallel rays into one which focusses the surfaces of the black and colourless glasses bounding the air-film, and the little silvered ring borne at the centre of the latter. This ring and the interference bands, which are localised in the film, and also the pair of vertical parallel spider-lines and single horizontal line of the micrometer, together with the serrated edge of the latter provided for rough measurement, will all be clearly focussed, if the conditions have been arranged as described, a complete circle of bands filling the field. Removal of the front lens of the Ramsden micrometer ocular reconverts the telescope to one for infinity, and thus enables one to review the adjustment of the images. On reinserting the front lens the magnificent field of dark and sharp interference bands, on the brilliant ground of red light, can be directly adjusted for the perfect verticality and amount of separation of the bands, by use of one or possibly two of the three black adjusting screws of the disc g_2. A convenient width is one which produces about a dozen bands in the field. They should be perfectly straight lines and strictly parallel, and thus any one of them can be readily brought to lie wholly between the conveniently separated pair of vertical spider-lines, the silvered ring being of such a diameter as causes it to show a little chord outside each of the spider-lines. Fig. 891 on page 1311 of "Crystallography," Vol. II, shows the appearance of the field. If the red field be not evenly lighted it is because either the vacuum tube or the telescope, or both, require a little adjustment by the centering screws provided in each case; in the case of the telescope it is the side-to-side screw that requires attention. If the focus of the silver ring be not perfect, the use of the back-and front centering screw at the foot of the telescope pedestal will effect the desirable sharpening. The height of the telescope can, of course, be adjusted so as to cause as much of the field of bands to be in view as is desired or convenient, as regards the vertical direction. The author prefers to screen off the lower third of the field by means of the serrated diaphragm scale, and thereby to eliminate a violet ghost of the semicircular opening at the common focus of objective and simple eyepiece, which is formed by reflection from one of the lens surfaces of the achromatic objective. This ghost is got rid of by slightly

inclining the objective in its cap, made adjustable by four little screws. The tilt is arranged so as to be just sufficient to throw the ghost below the serrated edge of the micrometer; the two-thirds field then left visible is absolutely perfect.

A perfect field of interference bands suitable for measurement and observation having thus been obtained, in red hydrogen light of the wave-length 0·0006562 mm., the endless screw which drives the fine traversing screw of the microscope may be thrown into gear, by raising the spring lever which permits it to engage with the worm wheel of the fine screw, and the large driving wheel (moving the endless screw by the connecting flexible shaft) worked with the left hand, when the bands will move parallel to themselves and to the spider lines, with perfect steadiness, as fast or as slowly as desired. Indeed, the control by the big wheel, and the efficiency of the flexible shaft which connects it with the endless screw-head, are so satisfactory that the bands can be held for any length of time at any position, the arrest of the band movement following that of the wheel to within a quarter of a band width in one second of time, or to a tenth of a band in two seconds, after which the movement stops dead.

In order to produce the interference bands in greenish-blue F-hydrogen light, when they are somewhat closer together corresponding to the shorter wave-length 0·0004861 mm., it is only necessary to rotate the constant deviation prism by means of the tangent screw in that direction which shortens the wave-length, when the green field will come into view and can be centred without trouble. The field of bands is particularly beautiful in this greenish-blue light. Further rotation will eventually bring in a field of bands in violet hydrogen light, corresponding to the line near *G*. But the light is, of course, feebler, in this less illuminating radiation.

If it be desired to produce the bands in yellow neon light, the hydrogen vacuum tube is replaced by a neon tube (a second adjustable fitting carrying it is provided, ready to slip on over the side tube after detaching that carrying the hydrogen tube), and the constant deviation prism adjusted to the position corresponding to this yellow radiation of wave-length 0·0005852 mm. As the prism circle is divided, it is only needful to determine once for all the reading corresponding to any particular spectrum line used for interference band production, in order to be able at once to set the constant deviation prism to the correct position for such radiation. If a cadmium vacuum tube be used, it is necessary to heat it to a temperature between 200° and 250° C., and the radiations corresponding to the red, green and blue lines are suitable for inter-

ference work, especially the very perfectly (quite unresolvably) monochromatic red radiation, the only rival to which in unresolvability is the yellow neon radiation.

For all ordinary purposes, with an air-film less than two millimetres thick, a hydrogen vacuum tube is most useful, using either the red or the green C or F-light. With a mercury vacuum tube, using the yellowish green radiation of wave-length 0·0005461 mm., the surfaces may be as much as a centimetre and a half apart without the bands disappearing. But if further separation of the two surfaces producing the interference is required the only two radiations which are sufficiently pure, that is, composed of a single unresolvable spectrum line only, are the red radiation of cadmium and the yellow of neon, of the respective wave-lengths 0·0006438 and 0·0005852 mm. For most of the purposes of fine measurement for which this interferometer will be used, however, thin air-films alone will be needed, so that either red or greenish-blue hydrogen light or yellow neon light will be equally suitable, no heating of the vacuum tube being required in either case. The neon tube employed has a large bulb blown on one of the limbs of the H, as recommended by several recent authors. Sodium light is, however, quite unsuitable, the secondary interference of the light from the two well separated lines D_1 and D_2 of the yellow doublet causing periodic disappearance of the bands even with thin air-films. The red and greenish-blue hydrogen lines are very close doublets only just clearly resolved, indeed the two F lines are only 0·093 Å.U. apart.

In conclusion, it is only well to recall the fact, that the scale of interference bands is one of half-wave lengths, the passage of each band past the reference centre corresponding to a movement of the microscope, and of the black-glass surface which it carries, of half the wave-length of the light which is being employed to produce the bands. For the light has to traverse the air-film twice, in going from the colourless glass surface to the black glass surface, and in returning to the former, so that the thickness of the air-film is only half the path, and any change of thickness equal to half a wave-length corresponds to the next similar phase of light or darkness.

The band-width (the interval between the densest line of darkness of any one band and that of the next band) is readily divisible into a hundred parts by the micrometer, that screw being used which moves both the parallel spider-lines simultaneously, the other moving one only and thus varying their separation. The half-wave-length of red hydrogen light is 0·0003281 mm., or 1/3048 mm., or 1/77,419 of an inch. That of the yellow neon light is 0·0002926 mm., or 1/3418 mm., or 1/86,808 of an inch. The

measuring unit of the instrument is thus the 1/7,741,900 or 1/8,680,800th of an inch, according to which of these two sources of light is employed. That is, it is roughly the one eight-millionth of an inch.

The author desires to accord his most grateful thanks to Mr. James Simms Wilson, of Messrs. Troughton and Simms, for invaluable help in the design and construction of the whole apparatus, including the torsometer described in the next communication; and to Mr. Conrad Beck, for very special aid in connection with the microscope and the Grayson rulings.

A Wave-length Torsometer and its Use with the Universal Interferometer.

By A. E. H. Tutton, M.A., D.Sc., F.R.S.

(Received April 26, 1923.)

(Plate 15.)

The author has at last been able to fulfil his intention of extending to the determination of the torsion constants of crystals (and any other small bodies, unprocurable in large pieces) the accuracy and refinement of the measurement by wave-lengths of light.

It is comparable to the method of determining Young's modulus of elasticity by the bending of plates and bars, by the use of the interferential "elasmometer," which the author* described to the Royal Society in 1903. The torsometer now described, used with the universal interferometer described in the preceding memoir, does for torsion what the elasmometer does for bending, so that it is now possible to determine the whole of the elastic constants of crystals, which in the cases of crystals with minimum symmetry (triclinic) are no less than 21 in number, by the refined method of the half-wave-length scale of parallel and rectilinear interference bands, and their micrometrically determined fractions. The torsometer itself is a refinement of the instrument devised and used by the late Prof. W. Voigt†, in which the method of the

* Phil. Trans., A, Vol. 202, p. 143 (1904).

† An illustrated account of the Voigt apparatus will be found in the author's 'Crystallography and Practical Crystal Measurement,' new 1922 edition, Vol. II, page 1349 and fig. 901.

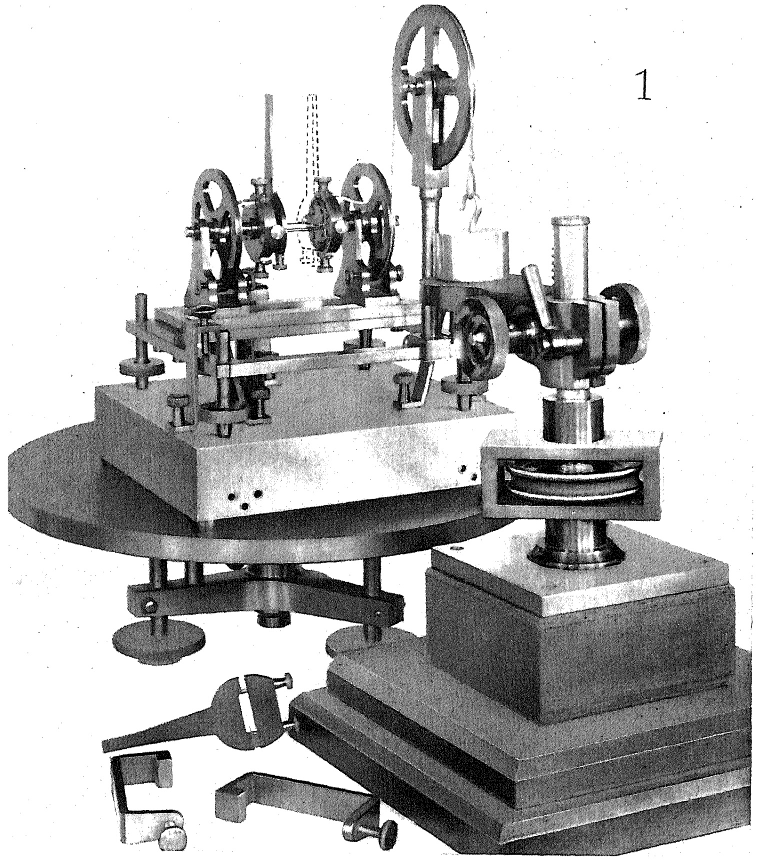

Fig. 1.—The Torsometer.

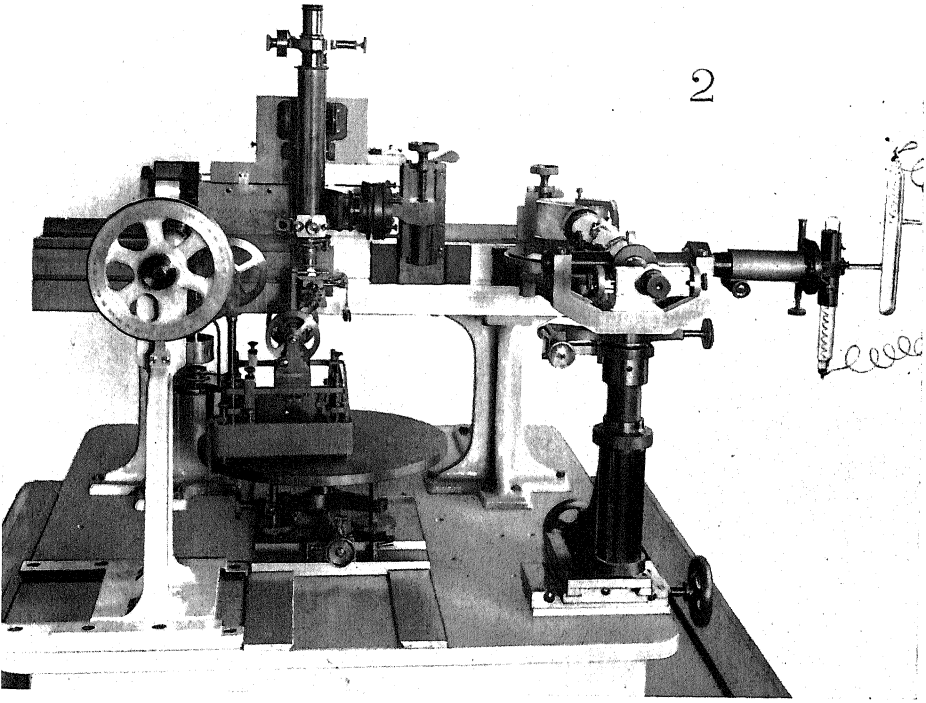

Fig. 2.—The Torsometer in Position on the Universal Interferometer.

optical lever was employed. The new torsometer transmits the torse movement instead to a Grayson-ruling signal, or fiducial mark, consisting of five engraved lines only one forty-thousandth of an inch apart, the movement of the central line of which is followed by the microscope and measured in interference bands, the torsometer being fixed on the work-table of the universal interferometer for the purpose. This is, indeed, the first practical application of the new interferometer.

The Torsometer is shown in fig. 1 (Plate 15), resting with the feet of its rectangular base on the round work-table of the interferometer. In general appearance it is very similar to the Voigt apparatus, but without the cumbersome power-delivering gear, and with the two mirrors, carried on the bar to be twisted near its two gripped ends, replaced by aluminium radials, the upper ends of which are to transmit their motion to the two Grayson-ruling sliders of the interferometer.

The apparatus for setting in action the weight, which effects the torsion of the object bar, is that used with the elasmometer, and is shown in operation on the right front in fig. 1, Plate 15. It consists of a little table for the support of the weight, this table being the expanded end of a thick rigid arm projecting horizontally from a stout boss sliding about a vertical cylinder, which is capable of a coarse movement up and down the cylinder by rack and double pinion motion, and fixation at any point by a clamping lever, and of a very fine vertical movement by a large driving wheel-nut gearing with a fine screw thread worked on a sufficient length of the lower portion of the shaft. The band from the torsion pulleys ends in a loop, and the platinised weights of 100, 200, 300, 400, and 500 grammes, which were specially made by Oertling for the author for use with the elasmometer, all terminate above in a hook instead of the usual bob, which is intended to rest in the string loop, when the weight is in operation. By means of the little adjusting table just described it is easy to allow the weight to fall as gently as may be required into the loop, in order to apply the torsion couple, and to take it up again when it is desired to take off the torsion.

The torsometer itself may now be described. On a rectangular bronze base, which can be firmly clamped on to the work-table of the universal interferometer by clamps supplied for the purpose (two being shown separately in the foreground of fig. 1, Plate 15), is mounted a stout rectangular frame, provided at each corner with a levelling screw of adequate length to afford about an inch of possible adjustment for height. After adjustment to that convenient height which brings the upper ends of the two aluminium radials just above the level

of the slightly rounded knife-edge ends of the little sliders which bear the Grayson-ruling fiducial marks, and the levelling of the frame by a spirit-level, the frame is clamped to the rectangular stand by three screw clamps of the arched type shown by the two which are clearly visible in fig. 1, Plate 15, the third (less clearly shown) fastening down the middle of the back bar of the frame. Four levelling screws are here better than three, as the frame is thus tightly clamped down so that no possible movement can occur. The frame bears a kind of lathe-bed parallel to its longer sides and somewhat nearer to one of them, screwed down rigid with the frame. In this bed slide the supports for the bearings of the duplicate pair of torsion pulleys, and for the chucks for the gripping of the object bar under torsion investigation. These two pulley-and-chuck fittings are duplicates in every sense, but reversed, the pulley-ends being outside and the chucks inside facing each other, conveniently for gripping the two ends of the object bar. Hence, either can be used as the torsion delivering pulley, while the other pulley can be fixed, being clamped between two milled-headed screws operating through the two columns (widened at the base) forming the bearing pedestal. Also each pulley-and-chuck fitting can be rigidly locked to the lathe-bed, by a large milled-headed screw operating from below. Each pulley has a band-groove in its rim-periphery, for a driving band of the most pliable yet strong silk cord, which can be passed through a radial hole in the rim at the end of a horizontal radius and secured there by a knot on the inside of the rim. In the case of that pulley which is chosen to deliver the twisting force, the band is passed downwards after its exit from the outer end of the hole, round the lower half of the pulley, and thence upwards to the larger pulley on standard. The boss of this standard is capable of sliding along the frame-bar, so that it can be fixed by means of a milled-headed binding screw at the position which brings it opposite to the torse-producing pulley, when the bar to be twisted is gripped in position by the chucks.

All three pulleys are constructed with conical axle pins, bearing in well-oiled conical-axial borings, the pins being adjustable screws worked by capstan heads, and secured by check-nuts in such a manner that no slacking back of the axles can occur, and that friction is reduced to the very minimum possible. The pulleys rotate with the slightest touch when the adjustments are properly made and the clamping screws are out of action.

The chuck for gripping the object bar is in each case carried at the end of a cylindrical bearing, itself rotating over a prolongation of the inner axle pin, the bearing and its chuck being rigidly attached to and moving with the pulley by means of a connecting bracket, which permits of about 140° of rotation of

the pulley and its chuck on each side, more than ample for any amount of torsion which is ever likely to be experienced. The chucks are obviously of great importance, as they require to be able to grip the object bar firmly yet without crushing or fracturing it, and to permit of and assist in its adjustment so that its axis is identical with (forming the middle part of) the straight line containing the two pulley axles. The nature of these chucks, and the circular heads in which they work, will be clear from fig. 1 (Plate 15), one of the radials (indicated in dotted lines) being removed when the photograph was taken, in order to reveal the chuck. They each comprise two opposing rectangular pieces, sliding dove-tailed in guides, flat-ended at those terminations which meet one another in the horizontal diameter of the chuck-head, and bearing a central engraved line identical with the vertical diameter of the head. Each is moved parallel to this vertical direction, out or in, by means of a milled-headed screw, working through a spring-box to prevent backlash and to secure return, above or below the chuck-head in each case. The movement outwards leaves a central open space between the flat interior ends, in which the object bar can be inserted, and when the spring-screw is reversed the flat jaws close up again and grip the object bar, with a force which cannot exceed a safe amount, determined by the spring. The chuck-head itself bears engraved lines along its horizontal diameter, which enable the closing to be effected symmetrically to the common axis of the chucks and pulleys, as regards vertical adjustment. To enable the bar to be centred perfectly to this axis, the horizontal adjustment is effected by two simple screws passing horizontally and radially through the chuck-head, with milled-heads for their manipulation from outside the head, before the final tightening of the adjusted chucks is completed.

The shape of the aluminium radials will be clear from fig. 1, Plate 15, which shows one in position and the other (dotted in position) detached and lying in the foreground. The circular part, concentric with the chuck-head when in position, is divided horizontally into two halves. The upper part tails off upwards into the radial, the whole fitting being of plate aluminium sufficiently thick to be rigid and undeformable when pushing the Grayson-ruling slider. The central part of the other end (that is, of the diameter of the circular part) is bevelled equally on each side of the plate to a moderately fine knife-edge, which is to rest on and mark the termination of the object bar for torsion determination purposes. The outer parts of this base of the upper semicircle are fitted with two screw threads for the purpose of attaching by means of milled nuts the lower

incompletely semicircular part of the radial fitting, the screws being relatively long and thin, so as to pass through holes drilled through the thickness of the aluminium plate parallel to its surfaces. The diametral edge-face of this lower half is not bevelled, but planed perpendicular to the plate surfaces, so that when the object bar is in position between the two halves, the fastening screw-nuts being also screwed up over the projecting ends of the screws, there can be no sideways wobbling and no likely fracture of the bar. To be certain of avoiding cutting of the object bar the device employed by Voigt, of placing a strip of tin-foil along the upper face of the bar, is adopted. The two knife-edges of the two radials, one fixed near each end instead of the Voigt mirrors, then mark the tin-foil with two clear thin lines, which form the limits of length of the object bar, the torsion of which is measured by the radials. The distance d along which the fiducial mark slider is moved by the radial end, divided by the radius of motion (length of radial) r, affords the tangent of the angle of torsion θ, that is,

$$\tan \theta = \frac{d}{r}.$$

The exact distance r should be counted from the axis of the bar to the point where, at the initial position of the radial arm, the radial (near its end) touches the slider's edge-end, and this can be determined in millimetres once for all, at the beginning of any series of measurements.

Adjustment of the Apparatus.—The torsometer is shown in position on the work-table of the interferometer in fig. 2, Plate 15, and another view from the side is given in fig. 3, Plate 14, of the preceding communication. The torsometer is arranged and securely clamped by the two screw clamps on the work-table of the interferometer, in such a position as brings the two vertical radials conveniently into contact, near their upper ends, with the two sliders bearing (rigidly cemented down) the Grayson rulings, each radial opposite the centre of the blunt knife-edge end of a slider. The two sliders are arranged by the upper adjusting screw at such distance apart as corresponds to the length of object bar between the two radials, and one slider is arranged under the microscope, by use of the lower screw, with the five-ruling signal or fiducial mark visible in field and more or less focussed. The pulley at the end, to be regarded as the fixed end of the bar, is firmly fixed by the two side screws, while the other pulley is left quite free to rotate easily in its most carefully adjusted conical bearings, preliminary testing having assured freedom from all wobbling and other movement than pure rotation. The gripping of the object bar by the chucks

and by the radials should be reviewed and if necessary perfected, with great care to avoid fracturing the bar.

The flexible cord-band is then adjusted round the under half of that pulley which is left free to turn, and which is to apply the twist to the object bar, and thence upwards round the upper half of the larger auxiliary pulley on the standard. Its end hanging down from the latter in front terminates in the loop, in which the twisting weight is to be hung by its hook. Just above this loop, any small initial weight is fixed which it may be desired to use, adequate to overpower all resistance to the torsion movement in the way of friction or other disinclination to start moving, and to keep all taut and quite ready to move as soon as the torse couple is applied by dropping the hooked weight into position. For the purpose of conveniently adding this initial weight the little scale pans shown in fig. 2, Plate 15 (and in fig. 3 of the preceding paper) is provided, but it is discarded in fig. 1, Plate 15, where no initial weight is being used. The elasmometer fitting is then brought into position, as shown in fig. 1, Plate 15, with the particular weight to be used in the first determination, say the 100 grammes, supported on its little projecting cloth-covered table and with the hook of the weight inserted in the string loop, the latter being slack.

The Determination of Torsion can then be commenced, the observer standing at the left side of the whole apparatus, from which he can most conveniently look down into the microscope and also manipulate the weight release. The work-table is first very gently and steadily moved in the direction parallel to the traverse of the microscope, by means of the stiffly working side-to-side screw provided for that purpose underneath the work-table, so as to bring the Grayson-ruling signal (which had best have been visible somewhere in the upper half of the microscope field when the slider and radial were in contact) to the position in which the middle one of the five lines 1/40,000th inch apart becomes centred between the two parallel spider-lines of the micrometer, the radial and slider being in full contact. The movement of the rulings to the centre is, of course, caused by the radial pushing the slider forwards along its path, in the direction away from the observer. The counterpoising of the slider, by means of small shot in its little suspended pail, has been once for all so carefully adjusted that no strain whatever is placed on the radial. The slider may indeed be pulled away from contact with the radial, and then pushed back again into contact, when the central position will again be perfectly restored; this forms an excellent test of the perfection of all the adjustments, and is rather a feat, considering that a magnification of 3,000 is being employed.

The observer now leaves the microscope and comes to the front to attend to the interferometer. The interference bands are always more or less adjusted, and only a few finishing touches are required, in all probability, as soon as the vacuum tube is actuated; the telescope being in position and the constant deviation prism at the circle-reading corresponding to the red hydrogen or yellow neon light to be used. The final adjustment of the bands, for their width and verticality, is effected by use of the black adjusting screws of the interference disc g_2. The large driving wheel on the left front of the interferometer is also thrown into operation by raising the spring-lever which gears up the endless screw to the worm-wheel. All is now ready for following up any movement of the rulings-signal by the microscope.

The observer now goes round to the left side again, and begins the application of torsion to the crystal bar, by gently lowering the weight-supporting table until the hook of the weight rests in the string loop, looking all the time through the microscope and observing the movement of the signal-rulings as the radial, in moving with the bar, pushes the counterpoised slider along its bed. The coarse movement of the elasmometer fitting is usually adequately fine for this operation. If the weight be only a small one, such as 100 grammes, the rulings will probably have come to rest while still in the field, probably not far from its lower edge. But with heavier weights they will move out of the field in the observer's direction, the movement being slow or quick according as the release is effected slowly or more quickly. As soon as the full amount of torsion has been effected, due to the couple which the weight employed produces with a pulley of the radius used, the rulings come to a dead stop. The weight can now be taken up again by raising the adjusting table, without any movement of the rulings, as release of the torsion causes the radial to recede away from contact with the slider.

It now only remains to follow the rulings by the movement of the microscope, and thus to measure the distance they have moved, this being done by rotating the big wheel which drives the microscope and counting the bands as they pass the reference centre of the telescope. A second observer is quite unnecessary; for the counting of the bands can be made as slow as one wishes, the speed being that of the big wheel, and the control by the latter is so perfect that the bands can be stopped while the single observer transfers his attention to the microscope for a moment, as often as is needful or desirable. When the rulings are being finally centred again under the microscope the wheel is, of course, moved very slowly and eventually stopped, when the centering has become perfect, so that the final fraction of a band can be determined,

if one is not centred exactly between the telescope micrometer spider-lines when the middle ruling is centred under the microscope. The whole determination for that particular weight and that particular radial is then to be repeated several times for the sake of accuracy, and the values obtained, which may run to two or three hundred bands or even more, should be concordant within one or two bands at most. Each time a re-determination is started, it is only necessary to reset the rulings to the centre of the microscope spider-lines while the slider is in contact with the radial, and to observe the bands and determine the initial fraction, if one is not absolutely centralised between the two vertical spider-lines and the reference centre of the telescope.

When one is satisfied with the concordance of determinations with this radial, say, it is that where most movement occurs, near the free pulley applying the torsion, a similar set of measurements is to be made for the movement of the other radial, a smaller matter if it be the radial near the fixed end of the object bar. In order to bring this other radial into position for the determination of its movement, one can either use the same fiducial-mark slider, and then it is merely a question of moving the work-table and clamped torsometer by means of the other (front-and-back) rectangular adjusting movement screw, so as to bring the second radial opposite the centre of the slider end, which is best pushed well out of the way while this is done, and then subsequently of adjusting the slider to contact with the radial and the rulings to the micrometer centre, the latter by use of the side-to-side rectangular movement, as for the first radial. Or one can use the second slider, two being provided to meet the case, and this then also requires to be brought under the microscope by use of the lower adjusting screw (which moves both sliders simultaneously) of the rulings-fitting.

The author has carried out by the above method some determinations of the torsion coefficients of fluorspar and rocksalt, using bars of the crystals of rectangular section, which have been specially cut and polished for the work by Hilger, parallel to the cube faces and to the rhombic dodecahedron faces, and the results will be communicated later, when they are quite complete. The work has proved the excellence of the method, and the perfect success of the apparatus now described.

The torsion coefficient T, according to Voigt, is afforded by the following formula :—

$$\theta = \frac{3\mathrm{TNL}}{t^3 b\,(1 + \frac{t}{b} f)},$$

where θ is the angle of torsion, the tangent of which is given as already explained by the quotient of the distance d determined in the measurements (as the product of the number of bands by half the wave-length of the light employed in producing them) by the radius of motion r, the length of the radial from the axis of the bar and torsometer to the position where it touches the fiducial-mark slider; N is the rotation moment of the couple employed to effect the torsion; L, b, and t are the free length (between the radial knife-edges), breadth, and thickness of the bar of crystal or other object; and f is a function of the sectional dimensions b and t, which is constant when the ratio of b to t exceeds 3, a condition which it is advisable to follow, for then f can be eliminated by a combination of observations.

The length between the tin-foil marks made by the radial edges, L, and the breadth b, can very conveniently be measured by the measuring microscope of the elasmometer, and the thickness t by the thickness measurer described to the Royal Society with the interference dilatometer,* fig. 6 on page 338 of that memoir illustrating it. Moreover, full accounts of both the measuring microscope and the thickness measurer will be found on pages 1344 and 1319 of the author's 'Crystallography and Practical Crystal Measurement,' Vol. II of the new (second) edition (Macmillan). The two instruments are illustrated in fig. 898 on page 1340, and fig. 893 on page 1320, of that book.

A very complete discussion is given in Chapters LVII and LVIII of the book, of the author's method of interferometry, from which any further details desired and a discussion of the theory can be obtained. The universal interferometer and the torsometer were under construction, however, when the book was published, so that only forecasts of their nature could be included.

The torsometer has been admirably constructed by Messrs. Troughton and Simms, the makers of the interferometer described in the last communication, and also of the elasmometer, interference dilatometer, and interference comparator for standards of length.

* 'Phil. Trans.,' A, vol. 191, p. 313 (1898).

The Measurement of Thermal Conductivity.

(Communication No. 1.)

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(The National Physical Laboratory.)

(Communicated by Sir Joseph Petavel, F.R.S. Received March 27, 1923.)

I. Introduction.

A knowledge of thermal conductivities has now become of importance in a variety of industries; for example, in the designing of electrical machinery and in the lagging of refrigerating and high-temperature plants.

While the literature* on thermal conductivity is fairly extensive, little attention has hitherto been paid to the design of apparatus for accelerated precision tests. For example, the ingenious methods of experiment devised by Prof. Lees† in the course of his classical and extensive investigations, while admirably adapted for the particular object he had in view, would be somewhat laborious if the number of specimens to be studied were considerable. Thermal conductivity is a physical constant not capable of ready determination by simple appliances, and in the design of the apparatus described later our aim has been to produce an equipment which will give the desired data with the minimum expenditure of time and labour.

The present paper is intended to be the first of a series of communications on thermal conductivity from the National Physical Laboratory, in which it is hoped to give the results of determinations on a variety of metals and poor conductors over a range of conditions, together with accounts of the several methods devised for the purpose. The present communication is devoted to a description of the technique developed for testing large numbers of materials of low conductivity, of which relatively small samples can fairly be taken as representative of the parent material. Special attention has been paid to the question of the measurement of the thickness of the specimens. The results of the conductivity measurements are given for a selection of materials and, in particular, for a number of timbers under definite conditions of moisture-content, etc.

* See Schofield, 'Glazebrook's Dictionary of Applied Physics,' vol. 1, p. 429, for a list of references.

† 'Phil. Trans.,' vol. 188, p. 481 (1892); vol. 191, p. 399 (1898); vol. 208, p. 381 (1908).

II. Description of Apparatus.

Three different apparatus (designated below as Nos. 1, 2 and 3) were designed to meet the various circumstances which arose. They are all modifications of the "plate" or "wall" method to which the standard equation defining conductivity (k)

$$Q = k A \,.\, t \frac{\theta_1 - \theta_2}{d}$$

is directly applicable. Q being the quantity of heat which, when the "steady state" is reached, passes normally in time t through a material of cross section A and thickness d, the faces of which are maintained at temperatures θ_1 and θ_2.

As regards the measurement of Q, the samples of material employed were all sufficiently thin compared with the cross section to make the use of a "guard ring" unnecessary. The edge correction could, if necessary, be determined with sufficient accuracy, and in any event its amount was small and usually negligible.

In each type of apparatus the "hot face" was a copper block heated electrically, the energy input being readily measured. The "cold face" was a copper block which was cooled by a stream of water flowing through a copper worm, the energy received being measured by the method of the continuous flow calorimeter. Thus a double measurement of the energy was made, and a valuable check was to hand which served to reveal any anomalies or adventitious losses which might otherwise have escaped detection.

The measurements of the time t and the area A presented no difficulties. The latter was the same in all three apparatus. The thickness d was sufficiently small in some instances to demand special arrangements for its determination. Some difficulty arose as to its measurement in the case of compressible materials like fabrics, for which a definite figure can only be given when the material is under a specific pressure. The question is dealt with in a separate section of the paper.

The temperature measurements (θ) were carried out by copper-constantan thermocouples and presented no special difficulties in themselves. One important question does, however, arise in the case of some materials, and that is the discontinuity in temperature which occurs at the two faces of a material unless there is first-class thermal contact with the adjacent hot or cold copper surfaces. In some cases the difficulty was met by amalgamating the copper plates, but this plan is not always feasible—for example, in dealing with porous materials. The point will be found to have received attention in the paper.

Other features which call for remark were the considerable variation in the physical properties of the various materials tested, *e.g.* the hardness, porosity, compressibility and in some cases the irregular structure. The several modifications of the apparatus devised, which we will now describe, were each adapted in the main for the study of a group of materials possessing the same general characteristics. Each of the apparatus required from 15 mins. to 30 mins., and less frequently 45 mins., for the specimens utilized to reach the steady state, so that measurements could be commenced.

The accuracy aimed at in the present measurements was 1 per cent., and this was achieved as a rule, though occasionally 2 per cent. was all that could be claimed. Some of the materials tested were, however, sufficiently indefinite in character to make this figure ample for all requirements.

It is convenient to measure power in watts, so that the above formula becomes

$$k\,(\text{c.g.s.}) = \frac{\text{Q (watts)} \times d\,(\text{cm.})}{\text{A (sq. cm.)} \times (\theta_1 - \theta_2)\,{}^\circ\text{C.} \times 4{\cdot}184}$$

In engineering practice in this country the conductivity unit commonly employed is the British Thermal Unit per hour per sq. foot per inch thickness per 1° F. temperature difference. To convert conductivities expressed in c.g.s. units into the British units it is necessary to multiply by 2903.

The use of "thermal resistivity" is found also to be convenient in engineering practice, where the term denotes the ratio of the temperature gradient (in degrees C. per cm.) to the watts conducted per sq. cm. To convert c.g.s. conductivity (k) into resistivity it is necessary to divide the reciprocal of k by 4·184.

(1) *Apparatus No.* 1.

(*a*) *General description.*—This apparatus was designed for the study of materials which were readily available in the form of discs $\frac{1}{2}$ mm. to 4 mm. thick and about 45 mm. in diameter. The apparatus proved specially convenient for those materials of a slightly compressible nature, such as cardboard and the various hard timbers which could not, moreover, be tested between amalgamated plates owing to the penetration of the mercury into the pores of the material.

The apparatus consists essentially of a hot plate mounted horizontally and midway between and parallel to two cold plates, two samples of the material under test being sandwiched in the intervening spaces (fig. 1). The hot plate was made up of two copper discs face to face, each 45 mm. ($1\frac{3}{4}$ inch) in diameter and about 1·25 mm. (1/20 inch) thick. Between them was mounted a heating

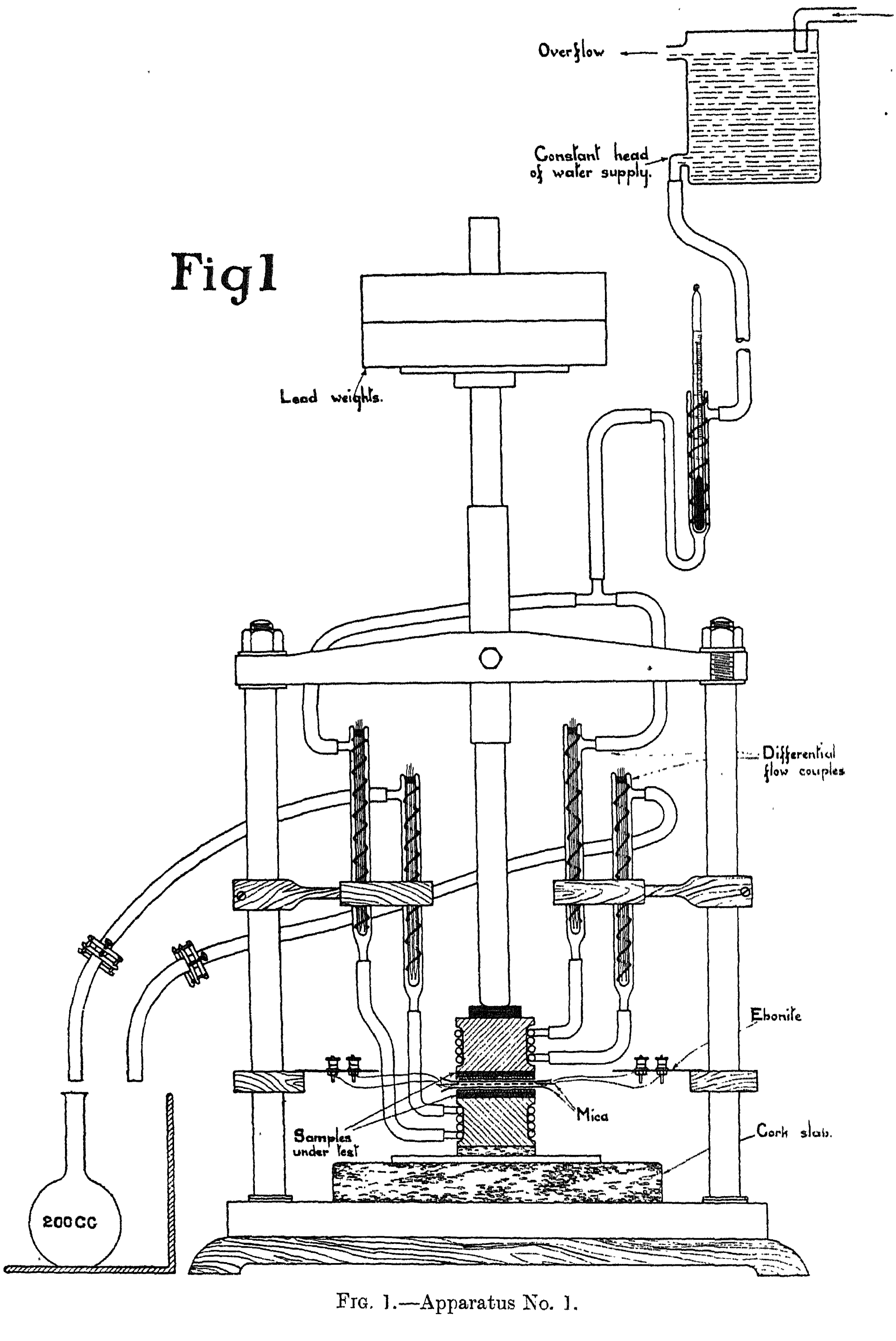


FIG. 1.—Apparatus No. 1.

grid made by winding 0·2 mm. platinum wire on a sheet of mica, the resistance when hot being about 8 ohms. The cold surfaces were provided by the ends of two short cylindrical copper blocks, each wound with a spiral of $\frac{1}{8}$-inch diameter copper tubing soldered to the surface of the block. The salient dimensions of the apparatus were those prescribed by the maximum current which could safely be passed through the heating grid, and by the ability of the cooling water to maintain a conveniently measurable temperature gradient across the particular thickness of test material employed.

The surfaces of both hot and cold plates were scraped flat to an accuracy of within 0·00025 cm. (1/10000 inch) over their area. Small holes were drilled into the edges near the flat surfaces, and into these thermocouples were pegged. The arrangement of the thermoelements is dealt with presently.

The water circulation was obtained from a constant head tank, the temperature of which was so adjusted by a submerged thermostatic heating coil that the mean of the inlet and outlet temperatures of the water circulation in the apparatus was approximately equal to room temperature, the object being to avoid the necessity of making correction for heat exchange between the copper blocks and their surroundings. The temperature rise of the water flowing round each block was measured independently by a pair of differential thermojunctions composed of six couples of copper-constantan connected in series and mounted as shown in glass tubes round which the water flowed through spiral guides. When observations were proceeding the apparatus was well wrapped up with asbestos and cotton wool, so as to maintain uniformity of temperature.

A known pressure was applied to the materials under test by the "dead weight" arrangement shown in fig. 1.

(*b*) *Measurement of the heat transmitted through the material.*—As already mentioned, both the energy input into the heating coil and the energy received by the two cold blocks were measured independently. If the conditions of the experiment are correct, then these two methods of measuring the heat conducted through the specimens should give results in close agreement.

It may be mentioned, however, that experience showed (with all three types of apparatus) that the figure for the useful energy input (E.I.) was usually slightly in excess of that derived from the energy transfer (E.T.) as measured by the water flow. The question is bound up with the control of the temperature of the inlet water and the elimination of the radiation losses from the cold blocks. The greater the care taken in this matter, the more closely did E.T. approach E.I. With proper precautions the agreement reached

1 per cent. or less. In the light of this knowledge, if for any reason (such as small heat flow) the disagreement between E.I. and E.T. somewhat exceeded this amount, the energy input figure (E.I.) was adopted with confidence.

The accuracy attainable when no special care was taken as to radiation losses is illustrated by the details of the several determinations quoted on p. 79. Similar details on p. 85 show closer agreement between E.I. and E.T.

The watts dissipated in the heating coil were measured on the same thermoelectric potentiometer as was used for the temperature measurement. This was effected by the arrangement of volt box and shunts illustrated in fig. 2, which is self-explanatory.

(*c*) *Temperature measurements*.—The thermoelements on the hot and cold

CIRCUIT FOR No. 1 APPARATUS.

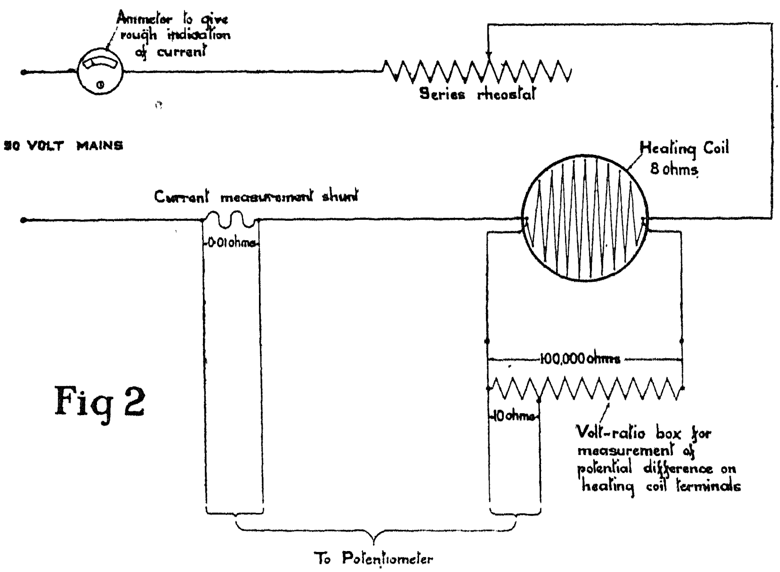


Fig 2

blocks were so arranged that the difference of temperature between the hot and cold faces, as well as the absolute values, could be measured directly. The arrangement of the circuits for effecting these measurements is shown in fig. 3.

The following typical observations show that the measurements were free from anomaly. The temperatures of the hot and cold surfaces were first measured independently and then differentially. Temperatures are expressed in microvolts. (1° C. = 40 microvolts approximately.)

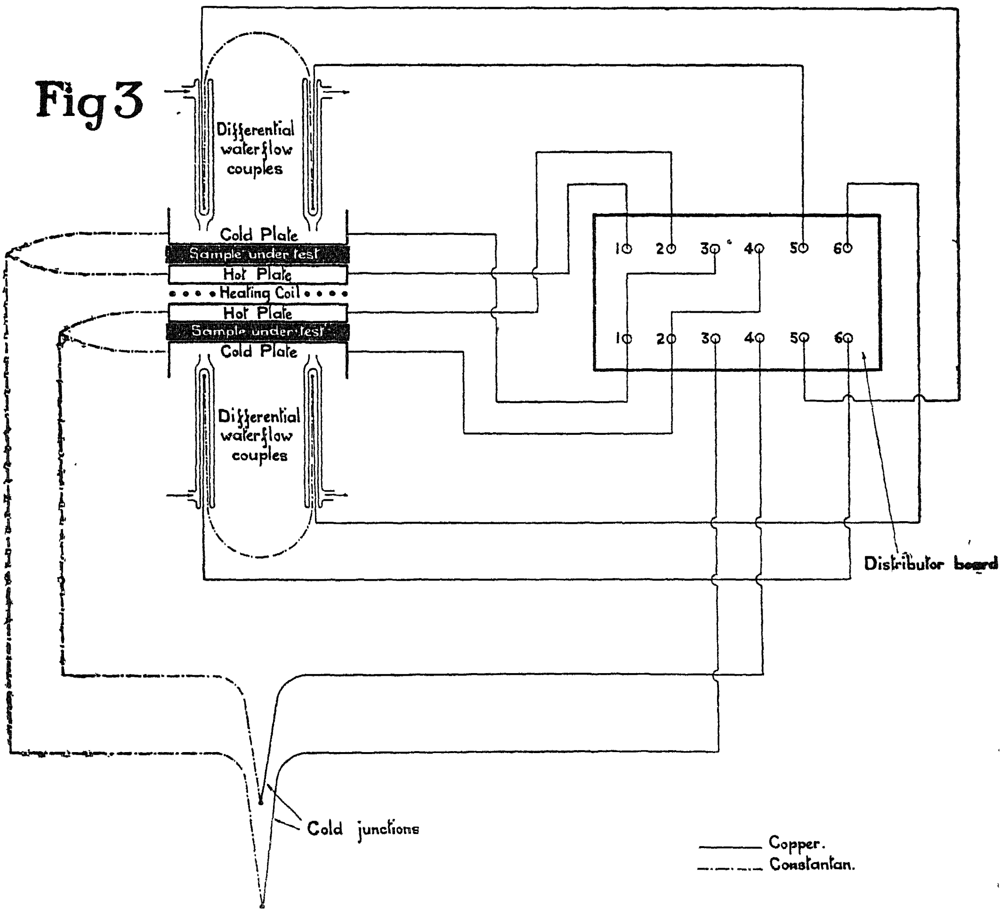
	e.m.f.
Direct measurements—	
Upper face of hot plate	1738
Lower face of hot plate	1739
Upper cold plate	714
Lower cold plate	706
Differential measurements—	
Difference between upper hot and cold plates	1024
Difference between lower hot and cold plates	1033

It will be seen that the differences between the hot and cold surfaces, obtained

N° I APPARATUS.

Diagram of Arrangement of Thermo-electric Circuit.

Fig 3



by differential measurements, are in exact agreement with differences calculated from the measured values of the hot and cold plate temperatures.

(*d*) *Correction for heat loss from edges of hot plate.*—A small correction has to be applied for the heat loss from the edges of the hot plate. This correction was obtained by taking observations with a series of samples of Balsa* wood of various thicknesses. This material had previously been tested in another type of apparatus of the guard-ring pattern and the absolute value of the conductivity determined. This value was then utilized in calculating the amount of energy transmitted through sheets of various thicknesses when tested in the apparatus shown in fig. 1. The difference between this transmitted energy and the total energy supplied to the heating coil is attributable to loss from the edge of the hot plate into the asbestos and cotton-wool insulation. This correction to the energy input should depend only on the difference of temperature between the hot and cold plates, and if this temperature difference be kept constant the energy correction should be independent of the thickness of the specimen under test, at any rate up to a certain limit. The data quoted below prove the validity of this assumption. The measurements refer throughout to the same sample, the thickness being progressively diminished.

Table I.—" Edge-Loss " experiments on Balsa Wood samples of various thicknesses. Constant temperature difference 5·6° C.

Thickness of Balsa wood in cms.	0·356	0·316	0·245	0·195	0·156	0·103	0·066
Correction for edge-loss in watts	0·05	0·04	0·04	0·04	0·04	0·03	0·05

(*e*) *Test of thermal resistance at hot and cold faces.*—A series of tests were carried out to determine the degree of excellence of the thermal contact at the hot and cold faces. These took the form of ascertaining whether increase of pressure had any effect in decreasing the thermal resistance. The material used for the tests was walnut, the heat flow being across the grain and tangential to the annual rings. The results are tabulated below in Table II.

It is seen that the above results differ among themselves by only 1 per cent. and that there is no definite dependence of conductivity on pressure. Hence it is assumed that with carefully prepared specimens the thermal resistance at the surfaces was negligible, since increase of pressure does not appreciably affect it.

* Balsa is the wood of a tropical tree. It is probably the lightest wood known, the material weighing from 6 to 9 lbs. per cubic foot. The thermal conductivity of the dry wood is extremely low, of the order of 0·00011 c.g.s. units, the value depending somewhat on the particular sample.

Table II.—Dependence of conductivity on pressure. Mean temperature 20° C.

Pressure lbs./in^2.	Conductivity c.g.s. units.
33·2	0·000327
46·1	0·000329
61·1	0·000328
52·0	0·000327
46·1	0·000330*
37·7	0·000328
33·2	0·000326*
23·2	0·000329

* Denotes repeat readings.

(*f*) *Test of Apparatus No.* 1.—Probably the most searching test that can be applied to the apparatus, particularly as regards the thermal contact at the bounding surfaces, is the comparison of the results obtained when samples of the same material in different thicknesses are tested. A study of the data in Table III, which are selected as typical, will show that the agreement between the results of tests on three different specimens of walnut, approximately $1\frac{1}{2}$ mm., 1 mm., and $\frac{1}{2}$ mm. thick, is quite satisfactory.

Table III.—Thermal Conductivity of various thicknesses of the same material.

The material tested consisted of samples of walnut cut adjacent to one another from the same section of the wood. The heat flow was across the grain and tangential to the annual rings. The experimental results are tabulated in full below :—

Pressure = 21 lbs./in^2. (1·48 kg./cm^2.).

Area of sample, cm^2.	15·59	15·59	15·59
Thickness of samples, cm.	0·0593	0·0913	0·1503
Difference in temperature between hot and cold faces, °C.	4·50	5·24	6·68
Mean temperature of hot and cold faces, °C.	20·6	21·2	18·2
Current in hot-plate heating grid, amps.	0·637	0·559	0·494
P.D. at terminals of heating grid, volts	5·200	4·550	4·040
Energy dissipated in grid, watts	3·310	2·542	1·996
,, ,, to each face of hot plate, watts	1·655	1·271	0·998
Correction for heat loss from edges of hot plate, watts	0·038	0·044	0·058
Hence useful energy leaving each face of hot plate, watts	1·617*	1·227*	0·940*
Mean rate of water flow in upper and lower cold blocks, c.cs. per second	1·205	1·047	1·395
Mean temp. rise of water in upper and lower cold blocks, °C.	0·311	0·286	0·158
Energy absorbed by water flow in each block, watts	1·570	1·251	0·922
Hence thermal conductivity c.g.s. units	0·000326	0·000328	0·000324

* Used in calculating the conductivity.

(2) *Apparatus No.* 2.

(*a*) *General description.*—This apparatus was designed primarily for those materials of which the contact resistance at the hot and cold plates is high and for which the use of amalgamated plates becomes necessary. The design of the mounting of the apparatus ensured the exact and easy assembly of the parts when the contact surfaces were flooded with mercury. The same apparatus proved also to be convenient for the study of the variation from point to point in the conductivity over the area of a large sheet of material, such as ebonite or micanite.

Manipulative difficulties arising from the use of heavily amalgamated surfaces made it expedient to use only one test sample, mounted horizontally between an upper hot plate and a lower cold plate. Further, the hot and cold faces aligned automatically so that the assembly of the apparatus was facilitated to an extent not possible with apparatus No. 1.

A study of fig. 4 will show how this was achieved. The hot plate constructed as in apparatus No. 1 is partially embedded in a block of ebonite with the exposed face amalgamated and facing downwards. The complete heating unit is carried on a spindle working in guides, and once it is properly aligned with the cold face, these guides ensure that the hot face always registers exactly with the cold face. This automatic alignment of the two surfaces was essential in the case of point-to-point tests on large sheets, and, of course, was particularly convenient when, as is described later, the degree of amalgamation of the surfaces was such that they were virtually flooded with mercury.

The cold surface was provided by the upper face of a cylindrical block of copper maintained at a constant temperature by a steady circulation of water through a water jacket, much as in apparatus No. 1. The temperature rise of the water was measured as before by a pair of differential flow couples.

A definite pressure was put on the test sample by the dead load shown in fig. 4, and asbestos and cottonwool-lagging were used as before.

(*b*) *Correction for heat leakage into ebonite mounting.*—Although it is possible to obtain the conductivity of a sample by observations of the temperature rise of the water flow, its rate of flow, and the temperature gradient through the material, it was deemed advisable to obtain, as heretofore, the energy by measuring the heat input. The watts supplied to the heating coil do not furnish, however, a direct measure of the heat flowing into the sample, since there is also a flow of heat into the ebonite in which the hot plate is mounted.

The magnitude of this flow was determined by observations on a sample of

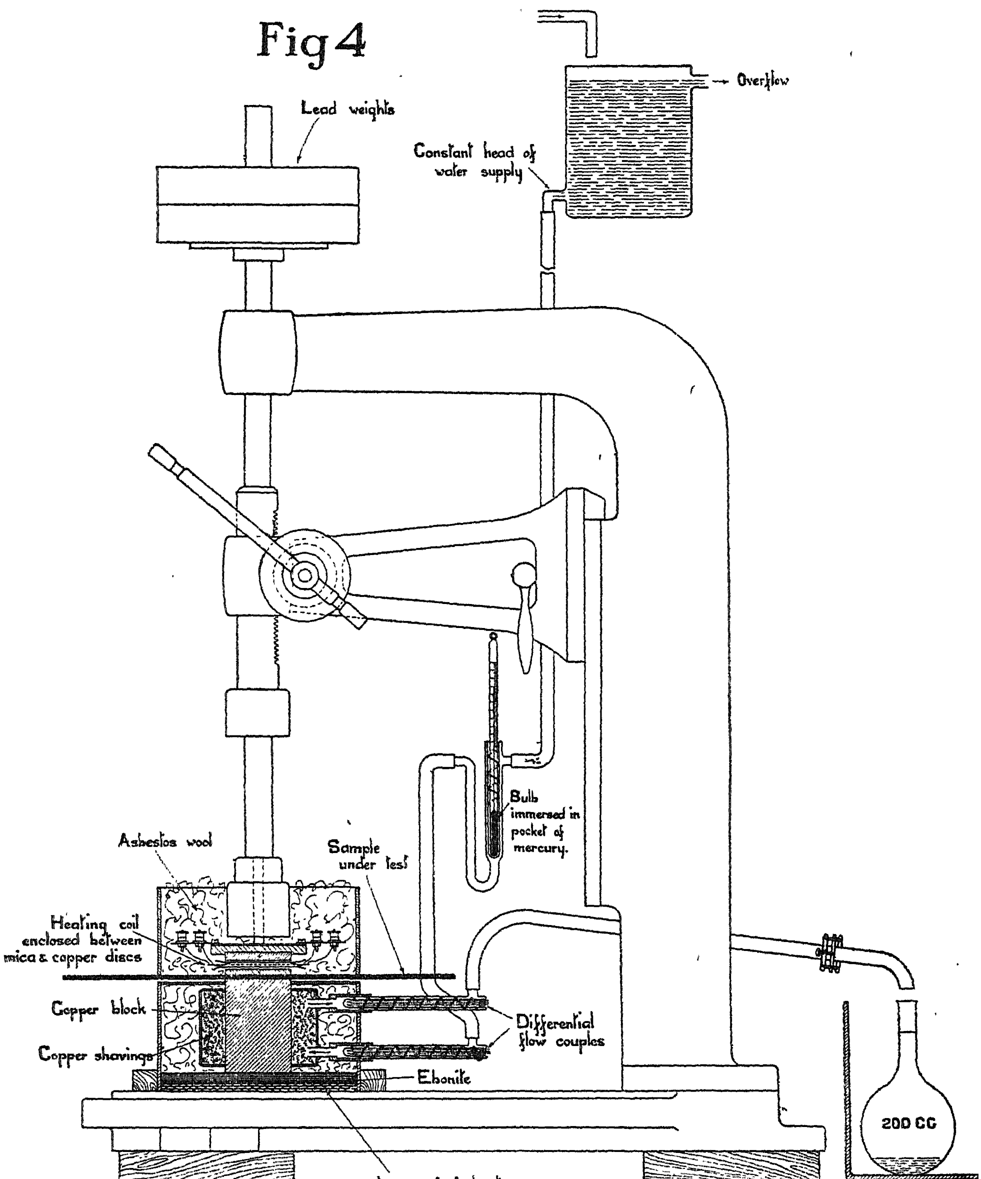


FIG. 4.—No. 2 Apparatus.

balsa wood of known conductivity and a table of corrections was drawn up. The magnitude of this correction can be seen from an inspection of the data below in the case of fibre :—

Table IV.—Correction for heat loss through the ebonite mounting in No. 2 apparatus.

Material tested : Vulcanised fibre.
Conductivity : 0·00066 c.g.s.
Thickness : 0·19 c.m.
Pressure : 21·0 lbs./in^2 (1·48 kg./cm.^{2}).

Temp.-diff. between hot plate and lagging (°C).	Total watts supplied to heating coil.	Correction for heat conducted through ebonite (watts).
13·3	3·88	0·78
23·3	6·57	1·25
54·4	15·32	2·96
82·2	23·10	4·50
35·0	9·46	1·89*

* Denotes repeat reading.

(*c*) *Experiments with amalgamated surfaces.*—When the surface of the material to be tested is somewhat irregular and hard or unyielding, amalgamated plates proved to be essential to effect good thermal contact between the hot and cold plates and the surfaces of the specimen. Even then it may not be possible to work with specimens of large area, as the following experiment shows :—

An apparatus was built up somewhat on the lines of apparatus No. 1, the two cold plates and the hot plate consisting of thick copper amalgamated plates each measuring 10 cm. × 10 cm. With these as contact plates, tests were made on a sample of material consisting of two sheets of mica each about 0·7 mm. in thickness, but which were known not to be uniform in thickness over their entire area. The results showed that the conductivity obtained was dependent on the pressure applied to the plates. The values for various pressures are given in Table V.

Table V.—Effect of pressure on conductivity of mica in large sheets.

Mean temperature 50° C.

Pressure lbs./in^2.	Apparent Conductivity c.g.s. units.
3·75	0·00088
16·25	0·00093
40·50	0·00100
75·00	0·00106

This large variation clearly proves that the surfaces of the specimens must be reasonably flat if the mercury on an amalgamated plate is to be relied upon for filling the cavities.

A further complication in these tests was the presence of gas pockets in the mica, which, of course, varied in dimensions with the pressure applied, and in fact, we were driven to the conclusion from a number of experiments, such as the one described above, that it was not possible accurately to test *large* thick samples of mica. It was found preferable to use thicknesses of the order of 0·025 cm., and in this thickness discs of mica of the necessary size accurate in thickness to 0·00025 cm. (1/10000 inch) can readily be obtained. With specimens of these dimensions the difficulties above described were non-existent. For example, tests were made on a sample of mica supplied in two thicknesses, 0·013 cm. and 0·025 cm. respectively. The results obtained were independent of the pressure and in good agreement, as will be seen in Table VI.

Table VI.—Conductivity of small specimens of mica.

Mean temperature 50° C.

Thickness of specimen. cms.	Conductivity c.g.s. units.
0·013	0·00135
0·025	0·00137

Experiments have also been carried out to ascertain whether the amount of excess mercury used on the amalgamated surfaces had an appreciable influence on the results. The material employed for this test was cardboard.

In the first experiment the amalgamated copper surfaces were flooded with mercury, the specimen inserted, and more mercury gradually added so as to form what were virtually two large flattened drops of mercury. When the hot surface had been lowered into contact, the excess mercury around the edges was removed.

In the second test no special care was taken to flood the surfaces; a few drops of mercury were placed on both copper surfaces, which, of course, were well amalgamated. The experiment was repeated several times, but no difference was observed, as will be seen from Table VII.

Table VII.—Amalgamation of surfaces.

Material: Cardboard.
Pressure: 21 lbs./in^2. (1·48 kgm./cm^2.).

A denotes careful amalgamation.
B denotes no special care with amalgamation.
* denotes repeat reading.

State of Amalgamation.	Conductivity c.g.s. units.
A	0·000610
B	0·000608
A	0·000612
A	0·000608*

(*d*) *Correction for the temperature drop through the mercury film.*—The thermal conductivity of mercury is only about 1/50th that of copper, so that a correction was necessary for the temperature drop through the two mercury films. This was obtained by direct experiment as follows. A disc of steel, 0·011 cm. thick, with flat polished surfaces and of the same diameter as the test specimens, was inserted between the amalgamated hot and cold plates and the temperature difference observed for various energy inputs in the heating coil. The temperature drop through the thin steel disc could be obtained by calculation from its known thermal conductivity, so the residue was attributable to the mercury film.

This method of obtaining the correction had the additional advantage that it automatically took into account any resistance at the liquid-solid surface due to microscopic gas bubbles. The magnitude of the correction can be seen from a study of the data in Table VIII.

Table VIII.—Temperature drop in mercury film.

Total Energy Input. Watts.	Observed temp. difference, °C.	Calculated temp. drop through iron sheet.	Temp. drop in mercury film.
48·15	0·52	0·07	0·45
179·20	2·10	0·26	1·84
175·70	2·00	0·26	1·74
311·00	3·40	0·46	2·94

To illustrate the order of magnitude of the quantities dealt with, a typical experiment with this form of apparatus is given below:—

(*e*) *Typical experiment with Apparatus No. 2 (amalgamated surfaces).*

Material : Commercial rubber.
Pressure : 8 lbs./in^2 (0·56 kgm./cm^2.).

Area of sample, cm^2.	15·59
Thickness of sample, cm.	0·286
Temperature of hot face, °C.	62·0
,, cold face, °C.	14·1
Correction for temperature drop through mercury film, °C.	0·1
Hence true temperature difference, °C.	47·8
Mean temperature of hot and cold faces, °C.	38·1
Current in hot-plate heating grid, amps.	0·5819
P.D. at terminals of heating grid, volts	12·550
Energy dissipated in grid, watts	7·30
Correction for heat transmitted through ebonite mounting, watts	2·45
Hence useful energy supplied to hot face of specimen, watts	4·85*
Mean rate of flow of water	200 cm^3. in 160 secs.
Mean temperature rise of water, °C.	0·925
Hence energy absorbed by water flow, watts	4·84

$$\therefore \text{Conductivity} = \frac{4 \cdot 85 \times 0 \cdot 286}{4 \cdot 184 \times 15 \cdot 59 \times 47 \cdot 8} = 0 \cdot 000445 \text{ c.g.s.}$$

* Used in calculating the conductivity. See p. 97.

(3) *Apparatus No. 3.*

(*a*) *General description.*—This apparatus is a somewhat specialised form of No. 2, adapted in the main for carrying out measurements on materials which are only available in very thin layers (for example, certain fabrics, micas and mica compositions), so that the heat transmitted for an appreciable temperature difference was very considerable. This necessitated the use of a heavier type of heating coil which was totally enclosed in the block of copper, as shown in fig. 5.

The specimen rested between the upper surface of this block and the lower surface of a water-cooled copper block of the type already described. When the specimen had been inserted between the blocks, pressure was applied by means of a spring plunger and the magnitude of this pressure determined by the scale reading. As previously, to reduce stray heat losses both the hot and the cold bars were enclosed in cases packed with insulating material.

In the experiments with this apparatus on materials of thickness from 0·002 cm. to 0·05 cm., no attempt was made to separate contact resistance at the surface from the true resistance of the material, as an "overall" coefficient is all that is desired for most purposes.

The same general precautions were taken as with the other two types of apparatus.

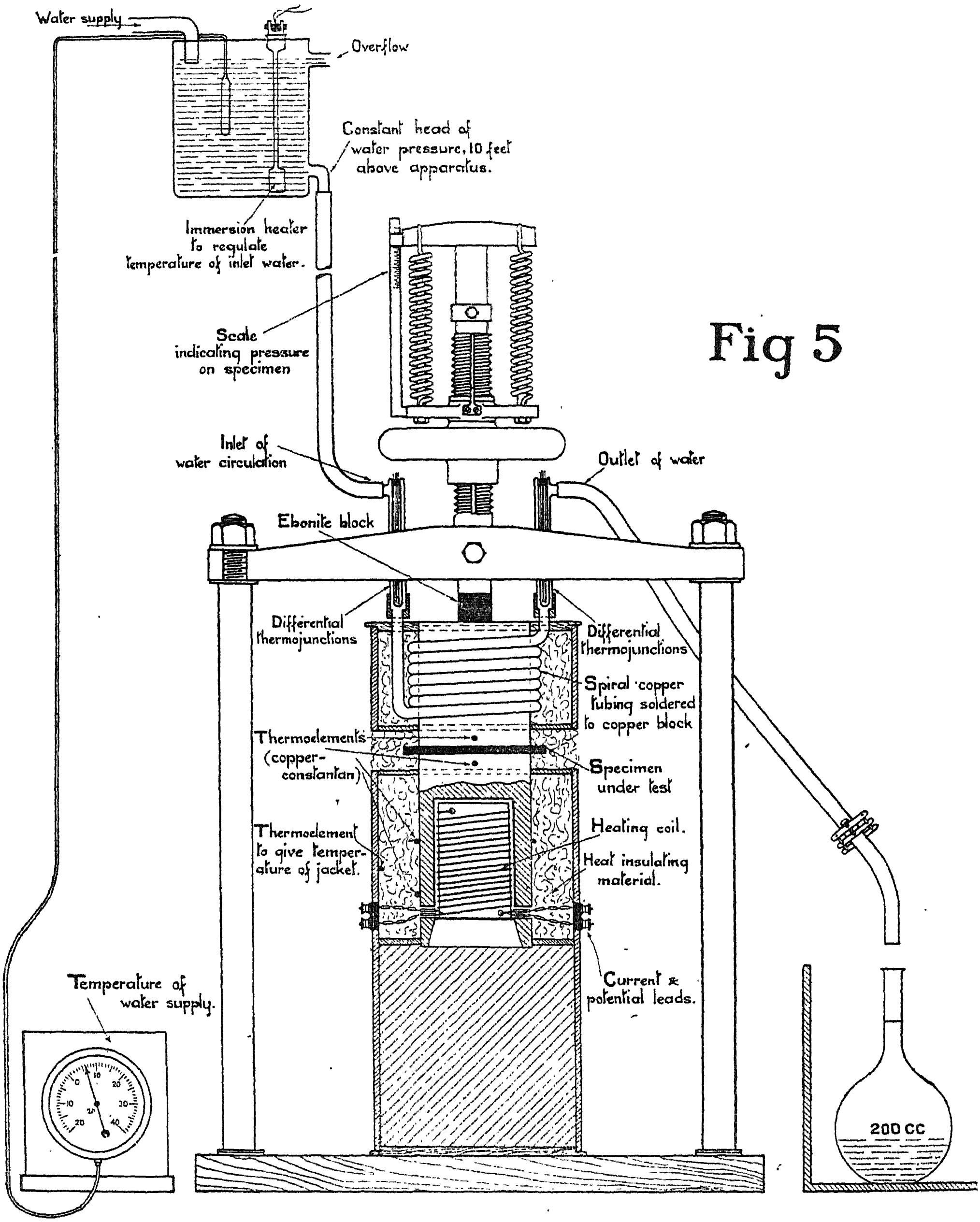


FIG. 5.—No. 3 Apparatus.

(*b*) *Effect of superimposing layers on conductivity.*—Measurements were made of the effect of superimposing layers on the conductivity. The data

given in Table IX and fig. 6 refer to waterproofed silk fabric. The methods of measuring the effective thickness of the superimposed layers under a specific pressure are described later (p. 91). It will be seen that the conductivity increases considerably as the layers are increased in number.

Table IX.—Superimposed layers of waterproofed silk fabric.

Pressure 8 lbs./in². (0·56 kg./cm².) ; unamalgamated plates.

No. of layers.	Thickness cm.	Mean temp. °C.	Conductivity c.g.s. units.
1	0·012	21·0	0·000340
2	0·025	21·0	0·000359
6	0·075	21·0	0·000415
9	0·111	21·0	0·000440
1	0·012	21·0	0·000342*

* Denotes repeat reading.

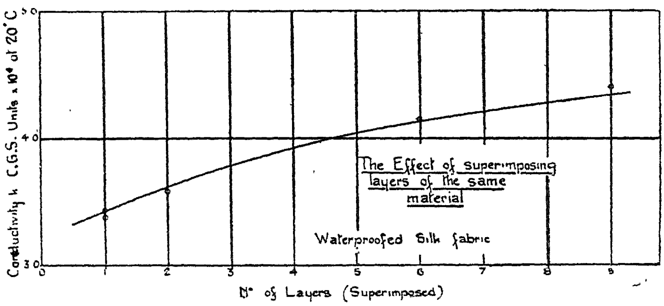


Fig. 6.—Effect on conductivity of superimposing layers.

(4) *Measurement of the Thickness.*

(*a*) *Description of apparatus.*—Considerable attention had to be devoted to the measurement of the thickness of the materials tested, more especially in those cases where this was dependent upon the pressure applied to the surfaces of the specimen.

For the thicker materials the apparatus shown in fig. 7 was used. It consists essentially of a micrometer head reading to 0·00025 cm. (1/10000 inch) clamped to a vertical pillar which carries also a fixed table. The specimen to be measured is laid on the table with a disc of steel resting on it. Both the surfaces of the table and the steel disc are accurately ground to plane surfaces. The observations are taken with and without the specimen between the plates. Pressure can be applied by the arrangement of weights as shown in fig. 7.

It was found that, as would be anticipated, the effect of a gradually increasing

pressure on compressible samples for the first time was to produce a permanent deformation, after which loading and unloading gave consistent results. From

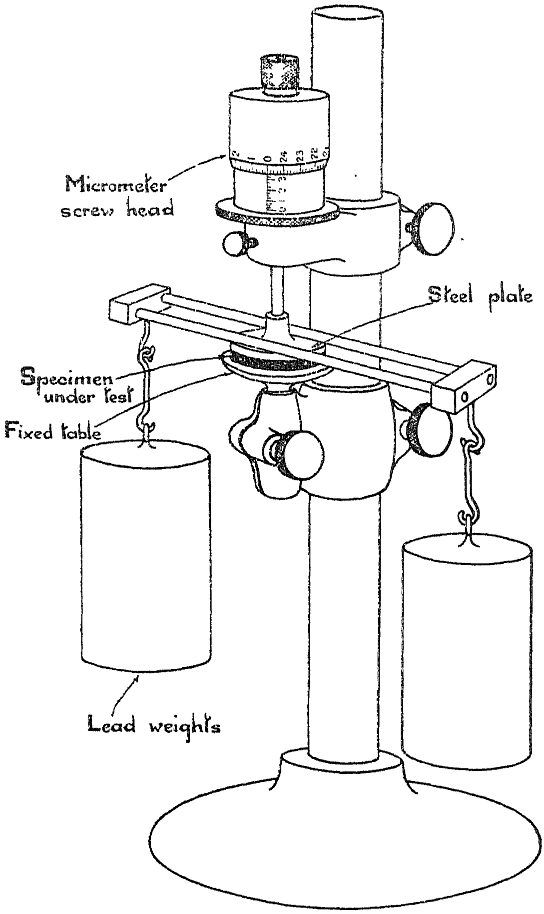


FIG. 7.—Apparatus for thickness measurements.

the pressure-thickness data it was possible to compute the thickness of the material under any load.

The above apparatus was not sufficiently sensitive for the study of thinner materials, such as paper and fabrics. For such measurements the apparatus illustrated in fig. 8 was employed and was an adaptation for the purpose in hand of a measuring machine designed and constructed in the Metrology Department of the Laboratory for the comparison of slip gauges.

The instrument is essentially a large micrometer with one of the headstocks carried on flexible supports. On examination of fig. 8 it will be observed that

the base of the left-hand headstock is supported by means of flexible steel strips at each end of the barrel, a method of support which allows the barrel to

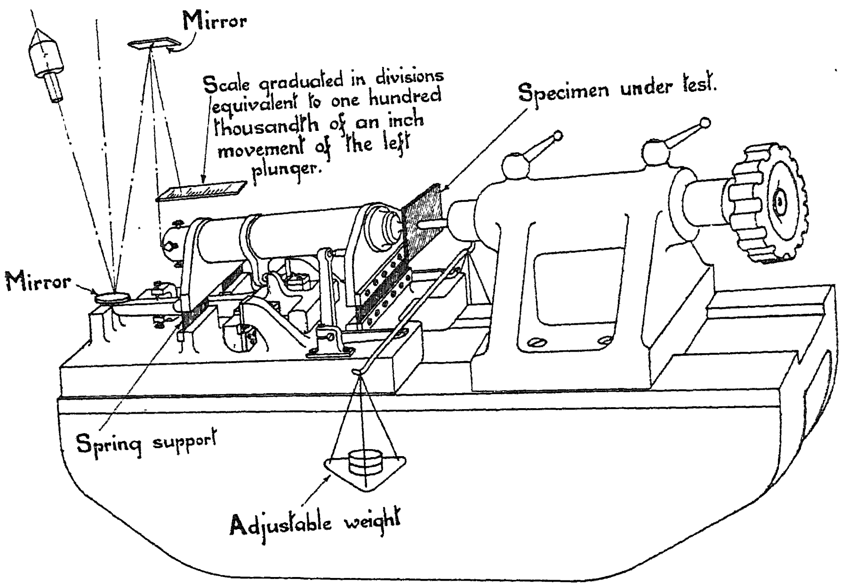


Fig. 8.—Apparatus for thickness measurements.

move backwards and forwards in a direction parallel to the bed, its axis remaining always parallel to itself. The measuring faces are $\frac{1}{4}$ inch in diameter and are adjusted to be parallel to the order of one-millionth of an inch. The pressure between them is derived from weights supended from two scale pans hanging on a cross bar, which force is transmitted to the barrel by two bell-crank levers placed one on each side of it. The magnitude of the pressure on the machine can thus be readily adjusted to any definite figure by varying the magnitude of the suspended weights.

The movement of the barrel is magnified partly by mechanical and partly by optical means, so that each division on the indicator scale corresponds to 0·000025 cm. (1/100000 inch). The mechanical part is performed by a 10 to 1 bell-crank lever. It may be mentioned that this lever is not supported on pivots, as the latter, however well made, would introduce some degree of friction or backlash. Instead, the lever has a virtual axis of rotation formed by the line of intersection of the planes of two pairs of steel strips, one pair horizontal and the other vertical, which are fixed to the lever and to the lugs on the base of the left headstock. (The perspective view of the machine in fig. 8 makes this arrangement clear.) The short arm of the lever, which is vertical, is furnished

with a hardened steel ball point, which rests against a flat hardened steel stop projecting from the base of the barrel. The face of this stop is arranged to be vertically above the virtual axis of the lever, so that no sliding contact (with consequent friction) takes place at this contact for small movements of the barrel, the motion being wholly of a rolling nature. The longer arm of the lever is horizontal and the vertical motion of its end is transmitted to a tilting mirror. To prevent undue straining of the suspension springs of the lever, its motion is limited by two stops as shown.

(*b*) *Change of thickness with applied load.*—The above machine was sufficiently sensitive to enable one to observe the changes which occur on loading and unloading a number of times in succession. A typical example is given in fig. 9, which deals with the case of balsa wood.

In working out conductivity data, the mean curve through the series of

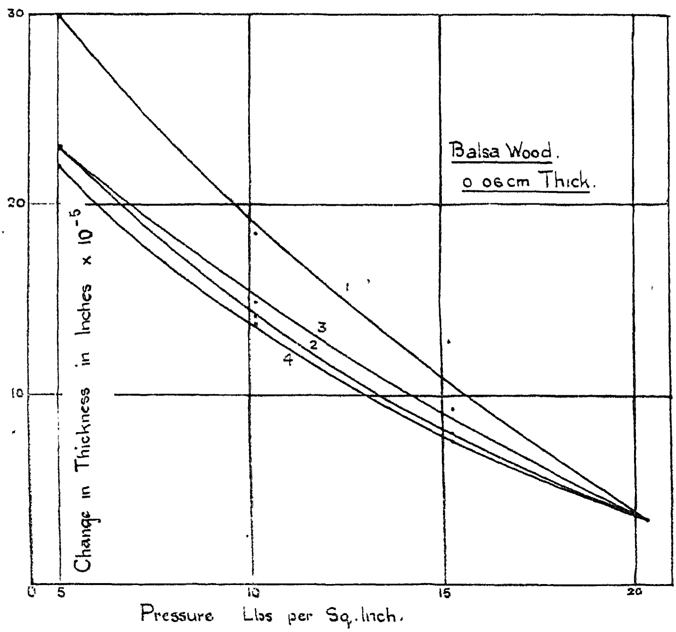


FIG. 9.—Relation between pressure and thickness for Balsa wood.

cyclical curves after the first loading was taken, so as to obtain the thickness appropriate to the applied load.

(*c*) *Combined thickness of a number of superimposed layers.*—The machine illustrated in fig. 8 was also used to investigate the variation in thickness from point to point over the area of a specimen, and the thickness of a number of superimposed layers, as compared with the thickness of an individual layer.

The results obtained in the latter series of experiments are of interest, as illustrating the degree of packing of the materials which takes place when a number of layers are superimposed. The tests were made to ascertain how the thickness of a number of layers of a sample superimposed compared with the sum of the individual thicknesses. The results for silk fabric and paper are given in Table X.

Table X.—Thickness of superimposed layers.

Pressure 20 lbs./in². (1·41 kg./cm².).

Silk Fabric. (Thickness of individual sheets.)	Thin Paper. (Thickness of individual sheets.)
cm.	cm.
$0 \cdot 0048_3$	$0 \cdot 0015_0$
$0 \cdot 0047_0$	$0 \cdot 0025_0$
$0 \cdot 0042_5$	$0 \cdot 0024_6$
$0 \cdot 0042_0$	$0 \cdot 0022_9$
$0 \cdot 0047_0$	$0 \cdot 0024_2$
$0 \cdot 0042_5$	$0 \cdot 0017_8$
$0 \cdot 0043_2$	$0 \cdot 0024_2$
$0 \cdot 0042_5$	$0 \cdot 0021_6$
Total ....$0 \cdot 0355_0$	Total ....$0 \cdot 0175_3$
Thickness of the 8 samples superimposed $= 0 \cdot 0292_1$ cm.	Thickness of the 8 samples superimposed $= 0 \cdot 0142_8$ cm.

It will be observed that the total thickness of the 8 samples of silk and paper is in each case some 20 per cent. less than the sum of the individual thicknesses, showing that very considerable packing takes place when the single layers are superimposed.

III. Results.

With the various apparatus described above a large volume of data has been accumulated concerning the thermal conductivity of a variety of materials. A limited selection of results is given below, and it is hoped that in the future the publication of the results for the remaining materials may present no difficulty.

The effect of pressure on the conductivity has already been considered as well as the effect of superposing layers of certain materials. Considerable attention has been paid to certain timbers, the relation between the conductivity and the direction of the grain and the influence of moisture content having been worked at.

We are indebted to the Superintendent of the Royal Aircraft Establishment,

Farnborough, for suitable specimens of a number of the woods, to the Industrial Rubber Products, Ltd., for specimens of commercial rubber, and to

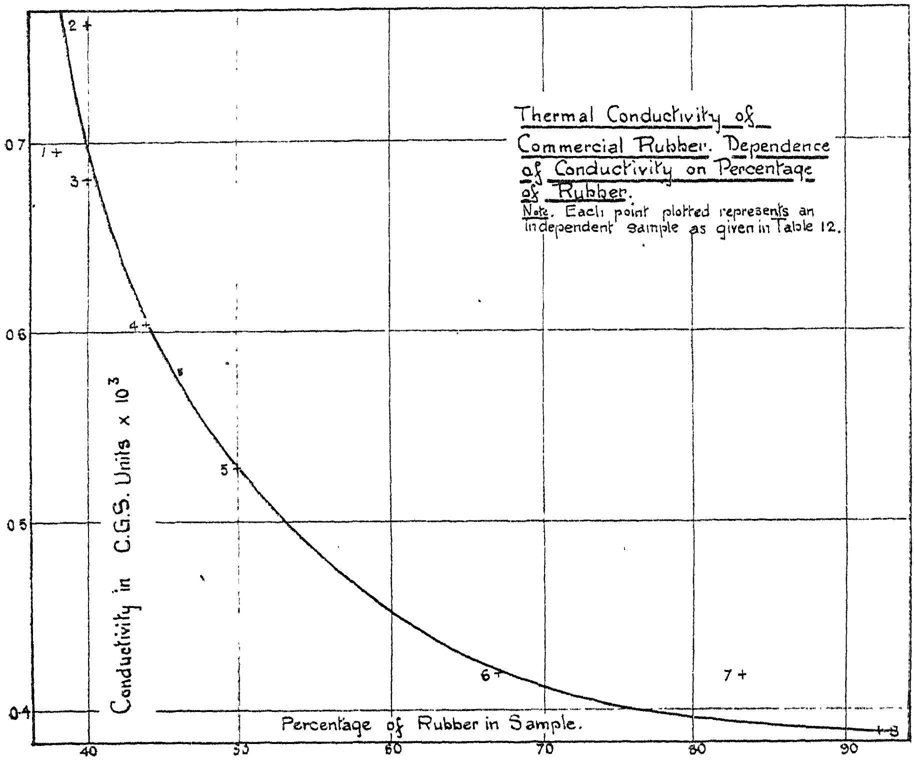


FIG. 10.

Messrs. Henry Wiggins for various specimens of mica. Fig. 10 shows the relation between conductivity and the figure for the percentage of rubber which was furnished by the makers. We understand that mineral matter forms the other constituents of the rubbers. The numerical results are quoted in Table XIII.

A few measurements were made on X-ray protective rubbers, which contain an admixture of lead oxide. No details of the composition were available, and as a rough guide to the amount of mineral matter present, the absorptive values for X-rays were measured in equivalents of lead. As might be anticipated the conductivity was found to increase with the lead equivalent.

(1) *The thermal conductivity of timber.*

(*a*) *Direction of heat flow and structure.*—The conducting power of a sample of timber is found to depend on at least two main features of the structure.

Firstly, the direction in which heat flow takes place, and, secondly, the coarseness of the grain, of which a notion is afforded by the number of annual rings per inch.

There are three approximately perpendicular axes of reference in a specimen of timber which are convenient to adopt:—

(1) Parallel to the grain or, more precisely, the fibres.

(2) Across the grain (or perpendicular to the fibres) and radial to the annual rings.

(3) Across the grain and tangential to the annual rings.

Our results (Table XII) go to show that in the case of the woods we have tested, the "longitudinal" conductivity ("with the grain") is roughly twice that of either of the "transverse" conductivities, and that, as regards the two latter, the "radial" conductivity is usually (and very approximately) some 5 to 10 per cent. greater than the "tangential" conductivity.

These results might be anticipated if we recall that in the direction of the grain the heat finds virtually an unbroken path of flow, as the annual rings (if present) consist of rings running longitudinally through the wood in continuous cylindrical bands concentric with the axis of the tree.

When heat flow takes place across the grain and radially to the annual rings, the path of flow, although largely obstructed by the fibres lying across the path, is supplemented by the medullary rays, which consist of bands of honeycomb-like cells radiating from the centre of the tree and interconnecting the annual rings. These medullary rays are invariably present, even though, as in the case of some tropical plants, the annual rings are not.

But in the case of heat flow across the grain and tangential to the annual rings, the path of heat flow is obstructed by both the fibres of the wood and the medullary rays, the result being a lower value of the conductivity than in either of the previous cases.

It may be added that the medullary rays do not interfere to any great extent with heat flow along the grain, since they are usually much wider in cross section measured longitudinally than transversely.

As regards the dependence of conductivity on the coarseness of the grain the coarser the grain the less dense will be the wood, since the fibres are less tightly packed, and the lower the conductivity, as our results confirm.

In fig. 11 the appearance of the annual rings is shown in the case of the specimen of ash. This was prepared by taking a "rubbing" of the end-grain with carbon paper, the facsimile being then either photographed or carefully traced by hand. The method has the advantage of showing the appearance of the

grain of the actual specimens employed. The positions from which the various test samples were cut are indicated in the figures. For instance, a circle

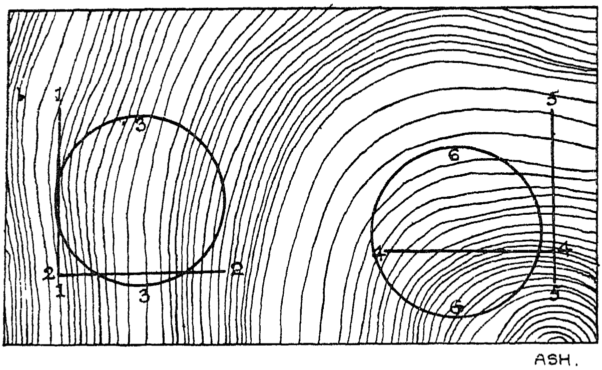


FIG. 11.—"Rubbing" of end grain of ash, showing locations of test specimens.

indicates that a disc $1\frac{3}{4}$ inches in diameter was cut from the position shown, the flow of heat taking place at right angles to the disc. A straight line shows such a disc in section, heat flow taking place perpendicular to that line.

The preparation of the test samples of the requisite thinness and parallelism of faces presented some difficulty at first, more especially when they had to be cut at right angles to the grain. The difficulty was emphasised with the softer woods. The plan eventually adopted was to plane or turn the samples roughly to size and finish off by rubbing with a fine carborundum stone.

(*b*) *The effect of moisture content on thermal conductivity.*—The effect of the moisture content on the elastic and other constants of timber is well known, and it was therefore thought that it would be of interest to find out to what extent the moisture content affected the thermal conductivity. Tests were accordingly made on a sample of spruce, the results for which are given in Table XI and fig. 12, the heat flow being across the grain and radial to the annual rings.

It should be mentioned that the sample was gradually dried out in an electric oven maintained at 100° C., measurements of the conductivity being taken with progressively reduced moisture contents. It may be added that the moisture contents are computed on the weight of the dry sample, so that if

W_1 be the weight of the sample before heating,
W_0 ,, ,, ,, after prolonged heating,

the percentage moisture content $= \dfrac{W_1 - W_0}{W_0} \cdot 100.$

The necessary precautions during weighing were taken, based on the experience of the Aeronautical Inspection Directorate of the Air Ministry.

Table XI.—Moisture Content and Conductivity.

Moisture Content per cent.	Conductivity c.g.s. units.
3·40	0·000292
5·80	0·000302
7·70	0·000308
9·95	0·000318
17·00	0·000340

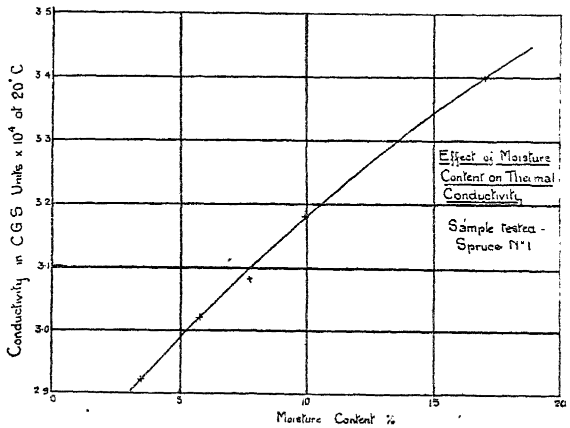


FIG. 12.

(2) *Results of thermal conductivity of timbers.*

Timbers tested in No. 1 apparatus (polished surfaces not amalgamated). Pressure = 21 lbs./in². (1·48 kg./cm².). The temperature drop across the specimen varied from 3° to 20° C. in different experiments. Not less than five determinations were made on each sample. The positions of the samples corresponding to the numbers in column 3 are as follows :—

Open grain—

(1) Heat flow across the grain and radial to the annual rings.

(2) Heat flow across the grain and tangential to the annual rings.

(3) Heat flow with the grain.

Close grain—

(4) Corresponding to position (1) above.

(5) ,, ,, (2) ,,

(6) ,, ,, (3) ,,

Table XII.

Timber.	Moisture content per cent.	Position.	Thickness cm.	Mean temp. °C.	Conductivity c.g.s. units.
Ash (Sp. Gr. = 0·74)	15·5	1	0·100	20	0·000365
				25	0·000381
	15·0	2	0·102	20	0·000369
				25	0·000371
	14·3	3	0·091	20	0·000714
				25	0·000725
	16·0	4	0·100	20	0·000464
				25	0·000469
	16·6	5	0·100	20	0·000416
				25	0·000420
	14·9	6	0·081	20	0·000754
				25	0·000771
Mahogany (Sp. Gr. = 0·70)	15·2	1	0·100	20	0·000391
				25	0·000398
	15·2	2	0·106	20	0·000351
				25	0·000354
	14·5	3	0·108	20	0·000701
				25	0·000716
	14·9	4	0·105	20	0·000416
				25	0·000419
	12·7	5	0·107	20	0·000387
				25	0·000392
	15·2	6	0·153	20	0·000776
				25	0·000790
Spruce (Sp. Gr. = 0·41)	17·0	1	0·147	20	0·000341
	16·9	2	0·150	20	0·000264
	15·9	3	0·151	20	0·000550
	16·2	4	0·150	20	0·000242
	16·2	5	0·159	20	0·000237
	15·4	6	0·152	20	0·000509
Walnut (Sp. Gr. = 0·65)	12·1	1	0·146	20	0·000346
	11·3	2	0·150	20	0·000326
	11·8	3	0·154	20	0·000794
Teak (Sp. Gr. = 0·72)	10·3	2	0·100	20	0·000314
		5	0.097	20	0·000341
Oak (Sp. Gr. = 0·60)	13·7	2	0·154	20	0·000280
Cedar (Sp. Gr. = 0·49)	13·4	2	0·230	20	0·000290
Cedar (different sample, Sp. Gr. = 0·48)	12·7	2	0·200	20	0·000252
Cedar (East African Pencil, Sp. Gr. = 0·48)	10·6	—	0·197	20	0·000277
Kiri (Japanese, Sp. Gr. = 0·32)	24·1	2	0·186	20	0·000210

(3) *Thermal conductivity of various materials.*

Summary of Results.

Table XIII.

Material.	Thickness cms.	Pressure lbs./in².	Mean temp. °C.	Conductivity c.g.s. units.
Ivory (African) (various samples) ⊥ axis	0·167 to 0·185	113	80	0·00108 to 0·00125
Ivory (African) (various samples) ‖ axis	0·178	113	80	0·00137
Quartz ⊥ axis	0·253	21	25	0·0147
,, ‖ ,,	0·253	21	40	0·0244
Ebonite (various samples)	0·035 to 0·15	21	25	0·00038 to 0·00044
Vulcanised Fibre	Various	21	50	0·0005 to 0·0008
Mica (various samples)	0·01 to 0·025	120	50	0·0010 to 0·0014
Micanite (commercial)	Various	21	30	0·0005 to 0·0010
Cotton fabric	,,	21	40	0·00018 to 0·0002
Silk fabric	,,	21	40	0·00010 to 0·00012
Paper (rice)	0·003	21	40	0·00011
Cardboard	Various	21	50	0·0004 to 0·0008
Cement, Portland (burnt)	0·42	21	55	0·0030
Commercial rubber (vulcanised)—				
Percentage of rubber—				
38	0·385	8·4	25	0·00070
40	0·381	8·4	25	0·00068
44	0·287	8·4	25	0·00060
50	0·387	8·4	25	0·00053
67	0·286	8·4	25	0·00042
83	0·412	8·4	25	0·00042
92	0·324	8·4	25	0·00039
100*	0·103	34	25	0·00032
X-ray protective rubber—				
Lead equivalent—				
0·35	0·173	2·5	20	0·00079
0·41	0·260	2·5	20	0·00087
0·43	0·463	2·5	20	0·00107

Material.	Sp. Gravity.	Moisture Content Per cent.	Mean Conductivity at 20° C. ‡	§	¶
Timber†—					
Ash	0·74	15	0·00073	0·00042	0·00039
Mahogany	0·70	15	0·00074	0·00040	0·00037
Spruce	0·41	16	0.00053	0·00029	0·00025
Walnut	0·65	12	0.00079	0·00035	0·00033
Teak	0·72	10	—	—	0·00033
Oak	0·60	14	—	—	0·00028
Balsa	0·1	13	—	—	0·00011
Waterproofed Balsa	0·1	13	—	—	0·00013
Pseudo Balsa	0·25	13	0.00029	0·00016	
Cedar	0·48	13	—	—	0·00027
Fir	0·6	15	—	0·00028	
Pitch Pine	—	15	—	0·00033	
Kingia Fibre	0·3 to 0·6	—	—	0·00018 to 0·00025	

* Plantation rubber crêpe.
† Pressure 21 lbs./in².
‡ Parallel to grain.
§ Perpendicular to grain, radial to annual rings.
¶ Perpendicular to grain, tangential to annual rings.

SUMMARY.

Three types of apparatus of the "plate" type are described for the rapid precision determination of the thermal conductivities of materials of low conductivity. Energy was supplied by electrical means, a measurement of both the energy entering and leaving the test specimen being made. Temperatures were measured by thermocouples. The samples were thin and no guard ring was required. An average time for the attainment of the "steady state" was 30 mins. or less, and the average accuracy of measurement of the conductivity was about 1 per cent.

Among the points dealt with in the paper are the thermal resistance at the bounding faces of a material, the effect of superimposing layers of compressible material, the measurement of the thickness of compressible material, the dependence of the conductivity of timber on structure and moisture content, the variation of the conductivity of rubber with mineral content, etc.

We wish to express our appreciation of the valuable assistance which Mr. A. R. Challoner and Mr. D. E. A. Jones have rendered in this work.

The Thermal Conductivities of Metal Crystals.—I. Bismuth.

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(Communicated by Sir Joseph Petavel, F.R.S. Received 8 May, 1923.)

(From the National Physical Laboratory.)

I. INTRODUCTION.

Interpretation of the thermal conductivities of metals yields an important test of the validity of any theory of the solid state. In applying the theory it is usually necessary to assume an ordered arrangement of the atoms on a space lattice. Now all the accurate measurements of thermal conductivity of metals have hitherto been made on bars which consist of a random arrangement of aggregations of small crystals possibly held together by intercrystalline layers of unknown structure and indefinite extent. It seemed important to compare the results so obtained with the more fundamental values yielded from specimens consisting of a single crystal.

Experiments have been carried out in the first instance on bismuth for the reasons that (*a*) it is comparatively easy to obtain large crystals, and (*b*) it is one of the few metals which does not crystallise in the cubic system.* It was thought that any discrepancies between the results for the single crystal and those for the aggregate state would probably be more pronounced in such a case than if a cubic crystal were used.

Experiments by Lownds,† Perrot‡ and Jaeger§ have shown that the thermal conductivities of bismuth crystals in different directions differ considerably, but their work is incapable of furnishing any evidence of the kind required since all three workers resorted to the well-known method of measuring the ratio of the axes of the elliptical figures formed by melting allow melting-point coating on the surface of the crystal. This ratio, which gives the square root of the ratio of the thermal conductivities in the two directions parallel and perpendicular to the trigonal axis, affords no information as to the absolute value of either of the conductivities.

It might be expected that the less difficult measurements of the electrical conductivity of bismuth crystals in different directions would have thrown light on the subject, but a study of the available literature reveals widely different results by different observers, who again appear to have been interested in the ratio of the two principal conductivities rather than in the absolute values. The question is at present being dealt with at the laboratory, and we hope to publish results later. It should be mentioned that from the data obtainable it would seem that the ratio of the two principal thermal conductivities of bismuth crystal is not equal to the ratio of the corresponding electrical conductivities||—a point of considerable interest.

II. Apparatus.

(1) *Preparation of Specimens.*

The bismuth crystals were prepared by Mr. C. H. M. Jenkins, of the Metallurgy Department, and we are indebted to him for ascertaining the technique of growing individual crystals of the requisite size. The crystals

* Bismuth crystallises with rhombohedral symmetry. The arrangement of the atoms in the crystal has been determined by the X-ray method by James, 'Phil. Mag.,' vol. 42, pp. 193–96 (1921).

† Lownds, 'Ann. der Physik.,' vol. 9, pp. 677–90 (1902).

‡ Perrot, 'Arch. Sci. Phys.,' (4), vol. 18, p. 445 (1904).

§ Jaeger, 'Arch. Sci. Phys.,' (4), vol. 22, p. 240 (1906).

|| See, for example, Lownds, *loc. cit.*, p. 689.

were subsequently annealed for some days. A complete analysis of the crystals revealed only 0·02 per cent. of lead, a trace of iron and no sulphur.

For the purpose of the thermal conductivity measurements rectangular specimens with parallel faces and true edges are essential. We owe much to the manipulative skill of Mr. H. A. Jones, of the Optics Division, who successfully overcame the difficulties arising from the brittle and "awkward" mechanical characteristics of the bismuth crystals.

(2) *Thermal Conductivity Apparatus.*

One of the "plate" types of thermal conductivity apparatus designed at the Laboratory primarily for materials of low conductivity* was modified and refined to make it suitable for use in the present case. A diagram of the apparatus is shown in fig. 1, which is self-explanatory. As will be seen, the specimen was mounted horizontally between an upper hot and a lower parallel cold plate. The hot plate consisted of a copper block mounted in an ebonite base and heated electrically by an enclosed heating grid. The cold plate was a copper block round which was soldered a spiral of copper tubing through which a stream of water flowed. When once the apparatus was correctly assembled, it permitted the easy and exact registering of the hot and cold faces. The energy conducted by the test specimen was measured both by the amount supplied to the heating grid and by the amount received by the stream of water.

The apparatus permitted the application of a definite pressure on the faces of the specimen. Experience showed that a pressure of 30 lbs. per square inch was sufficient to ensure good thermal contact, and this figure was adhered to throughout the tests.

(3) *Special Sources of Errors.*

The apparatus, as originally constructed, was designed for specimens of area about 15 square cms. and with thermal conductivities of the order of 0·001 c.g.s. or less. The largest bismuth crystals obtainable yielded specimens only about 1 cm. $\times$ 2 cms. in area, their conductivity being of the order of 0·02. The smaller area and the higher conductivity both increase greatly the difficulty in making accurate measurements. The diminished area means that smaller quantities of energy can be transmitted, and that heat losses become proportionately greater; also, with reasonable rates of flow of the cooling water, the rise of temperature is smaller, and thus any variations in the temperature of the inflowing water cause proportionately greater errors.

* See, Griffiths and Kaye, 'Roy. Soc. Proc.,' A, vol. 104, p. 71, 1923.

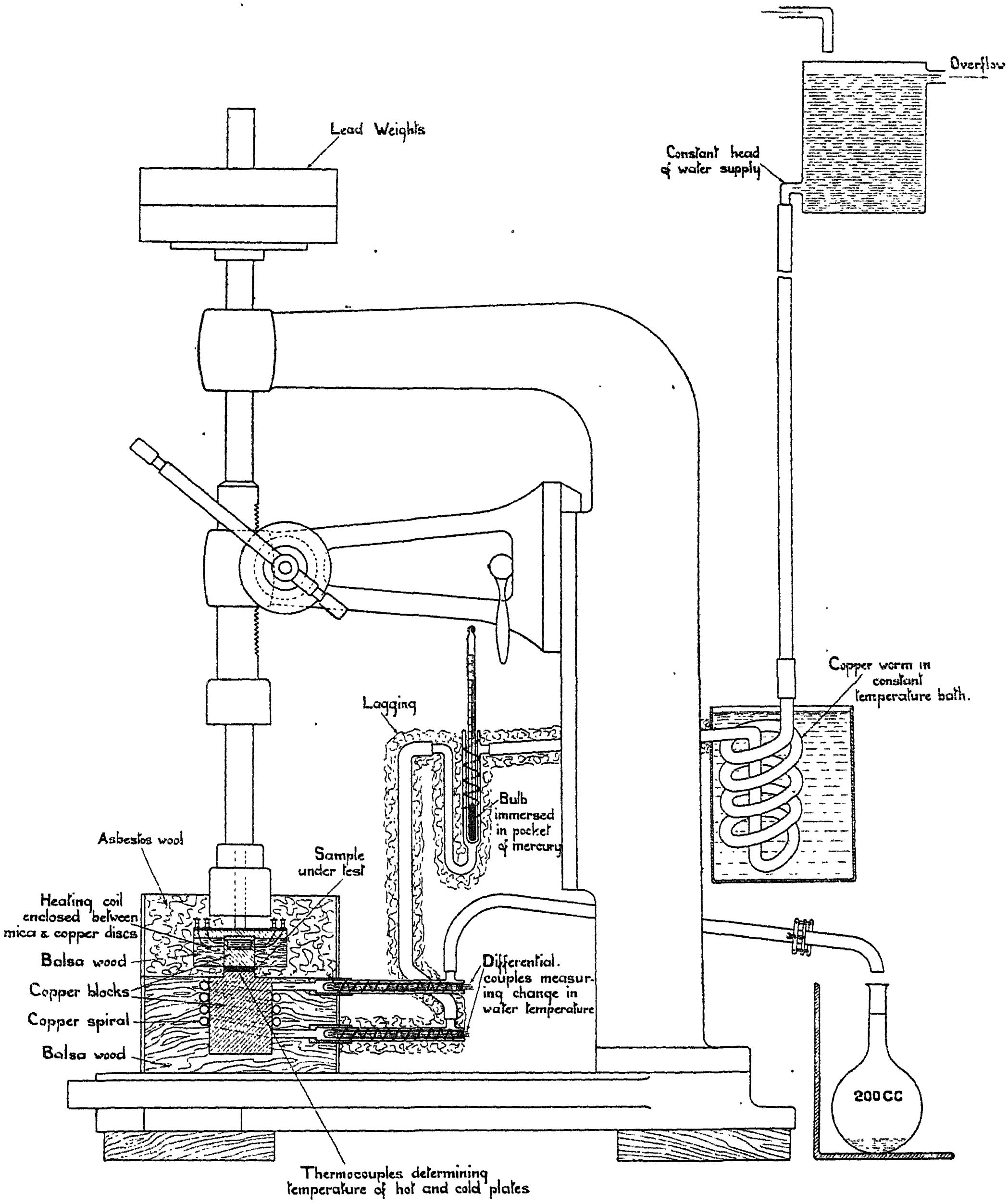


FIG. 1.—Apparatus.

The higher conductivity has the following effects :—

(*a*) For a given rate of transmission of energy the temperature gradient across the specimen becomes smaller. An upper limit to the power input is fixed by the dimensions of the heating grid.

(*b*) As the temperature gradient is smaller, any fluctuations in the temperature of the cold block, caused by variations in the temperature of the inflowing water, become more important.

(*c*) The temperature drops across each of the two surface films between the copper blocks and the specimen under test become proportionately larger.

(*d*) Uniformity of temperature over the surface of the hot plate becomes more difficult to ensure.

These difficulties were successfully overcome, and, as will be seen later, thermal conductivity measurements could be made with an accuracy of about 1 per cent. The average time for the apparatus to reach the steady state, so that measurements could be taken, was of the order of an hour.

(4) *Construction of Hot Plate.*

Preliminary experiments were carried out with a hot block of uniform rectangular section of the same area as the test specimens. The heating grid, which was furnished with both potential and current leads, was of platinum wire wound on a mica strip and insulated from the copper block by pieces of mica. The grid fitted in a rectangular slot cut in the copper block and this slot was covered with a plate of copper. The resistance of the current leads was negligible compared to the resistance of the grid itself. In these preliminary experiments the thickness of copper between the heating grid and the specimen under test was only 0·05 cm. Copper constantan thermocouples, which were pegged in the edge of the copper, indicated that differences of temperature amounting in some cases to more than one degree existed between different parts of the hot plate.

A new hot plate was therefore made, in which the heat from the grid passed through about 0·5 cm. of copper before reaching the surface of the specimen under test. The thermocouples placed near the edge of the hot plate were now found to differ by no more than 4 or 5 microvolts, so that the mean should be correct to about 1 microvolt (*i.e.*, 1/40° C.). In any event, it should be noted that any slight error thus introduced in measuring this temperature is eliminated in making the correction for the temperature drop in the surface film between the hot plate and the specimen. (*See* p. 108.)

(5) *Thermal Insulation of Hot Plate.*

It was feared that the substantial increase in the thickness of the new hot plate might seriously augment the loss of heat from the sides. In order to minimise this effect, the part of the hot plate projecting from the ebonite mounting was carefully encased in balsa wood, which was arranged to be nearly flush with the lower surface. Balsa is unsurpassed as a heat insulator, and the success of the plan is shown by the fact that, in spite of the ten-fold increase in the side area, the power loss at a given temperature was only increased on this score by about 20 per cent.

(6) *Construction of Cold Plate.*

The cold plate was made of copper rod 1 inch in diameter and about $1\frac{1}{4}$ inches long, round which was soldered a copper cooling spiral. The upper surface, which made contact with the specimen under test, was milled out so that a rectangular piece of exactly the same shape as the specimens projected about 0·1 cm. above the rest of the block. The thermocouples for measuring the cold-face temperature were inserted in the sides of this projection, so that they were as near as possible to the surface of the specimen. The whole cold plate was embedded in balsa wood.

(7) *Surfaces of Contact.*

The copper surfaces of the hot and cold plate were scraped flat to 1/10000 of an inch, and the surfaces of the test specimens were made optically flat. In the preliminary experiments the surfaces were flooded with mercury to ensure good thermal contact between the copper and bismuth. It was found, however, that the mercury amalgamated with the bismuth and so destroyed its surface. Apparently, the only course open was either to leave the surfaces dry or to use some liquid other than mercury to improve the contact. Choice was ultimately made of glycerine, the conductivity of which, while only 1/30th of that of mercury, is 10 times that of air. This proved satisfactory, as will be shown later.

(8) *Thermostatic Control of Temperature of Inflowing Water.*

Variations in the air temperature affected the temperature of the inflowing water, and the consequent changes in the temperature of the cold block made it impossible to measure accurately the heat passing into the water. This arose from the fact that (as in all continuous-flow experiments) any change in the heat energy stored in the system affected the rate at which energy was

received by the water. These temperature variations also made it impossible to attain steady temperature-distribution in the specimen under test. The inflowing water was, therefore, first passed through a copper worm immersed in a water bath with thermostatic control. The improved temperature steadiness which resulted made it possible to work with the small temperature gradients which obtained with the specimens of bismuth. Further, in spite of the small energy input, an agreement of the order of 1 per cent. was secured between the power input as measured (*a*) by the current and potential drop in the heating grid, and (*b*) by the rate of water flow and rise of temperature of the water. Before the introduction of the refined thermostatic control, the differences between the power measurements by the two methods sometimes amounted to from 7 to 10 per cent.

III. Measurements.

(1) *Measurement of Power.*

(*a*) *Power Supplied to the Heating Grid.*—The rate at which energy was supplied to the heating grid was determined by measuring by means of a potentiometer the potential drop across the grid itself and across a known series resistance, which latter afforded a measure of the current.

(*b*) *Loss of Power through Mounting of Hot Block.*—All the energy supplied to the heating grid did not pass through the specimen, but some of it was unavoidably lost through the ebonite and balsa-wood mounting of the hot plate. This loss was determined by making preliminary measurements on a sample of balsa wood of known thickness and conductivity (0·00011 c.g.s.) and of the same area as the test specimens. The total energy supplied to the heating grid was measured in the usual way. The small amount conducted through the sample of balsa wood could be calculated, and the remainder was therefore lost through the mounting of the hot block. The amount so lost was plotted against the difference between the temperatures of the hot plate and the air (Table I; fig. 2).

The test was carried out with two different thicknesses of balsa wood, the results of which were concordant. In the subsequent measurements on bismuth the corrections for power leakage on this score were obtained from fig. 2. It should be noted that only the portion of the graph lying between 0° and 10° temperature-excess was actually used in this way, though the observations at higher points were useful in plotting the graph.

(*c*) *Measurement of Power Received by Water.*—The heat received by the water was obtained by measuring the rate of flow of the water and the rise of

Table I.—Power Loss from Hot Plate through Mounting.

Thickness of Balsa wood.	Air temperature.	Hot-plate temperature.	Cold-plate temperature.	Difference between hot- and cold-plate temperatures.	Power conducted through balsa (calculated) (h_1).	Power supplied to heating grid (h_2).	Power loss from hot plate (h_2-h_1).	Difference between hot-plate temperature and air temperature.
Cms.	° C.	° C.	° C.	° C.	Watts.	Watts.	Watts.	° C.
0·203	16·00	35·75	17·60	18·15	0·09	0·44	0·35	19·75
0·203	15·70	42·90	17·65	25·25	0·13	0·66	0·53	27·20
0·203	15·75	64·40	17·70	46·70	0·23	1·23	1·00	48·65
0·122	14·85	33·20	17·55	15·65	0·13	0·50	0·37	18·35
0·122	15·15	33·85	17·55	16·35	0·14	0·50	0·36	18·70
0·122	15·90	62·30	18·10	44·20	0·37	1·37	1·00	46·40

temperature. The latter was measured differentially by six copper-constantan thermocouples in series, arranged so that the inflowing water was circulated

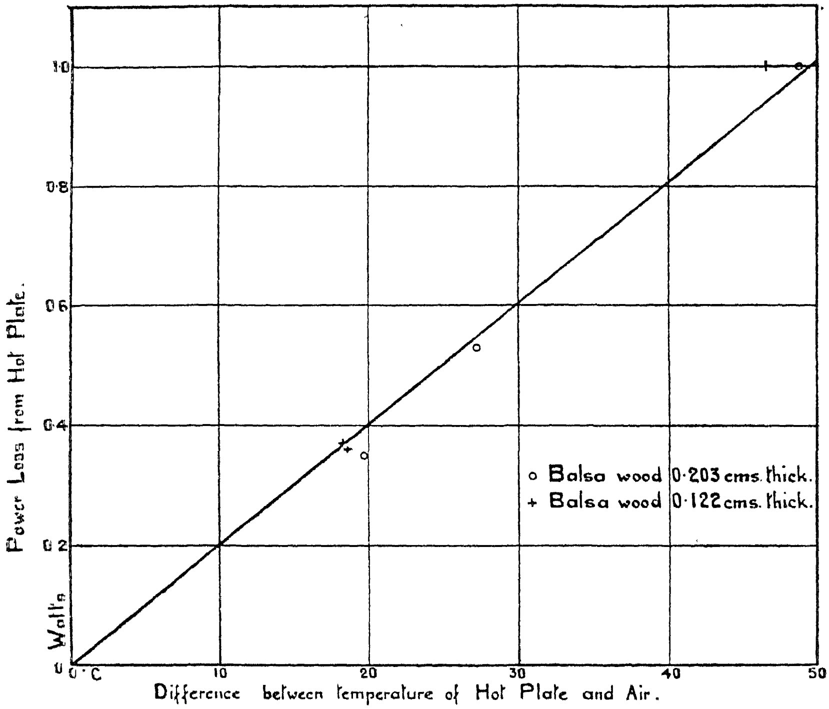


Fig. 2. Power Loss from Hot Plate.

round a glass pocket containing the cold junctions and the outflowing water round a similar pocket containing the hot junctions. The actual value of the temperature of the inflowing water was measured on a mercury in glass thermometer.

The heat losses from the water system take place (*a*) from the water tubing between the thermocouples and the cold block, and (*b*) from the cold block itself. For the purpose of determining these heat losses a specimen of balsa wood was inserted between the "hot" and the "cold" plates. No current was passed through the heating grid, but the arrangements permitted the temperature measurement of both plates as usual. The heat loss from the tubing was separately determined by "short-circuiting" the spiral round the cold block by a short length of rubber tubing and passing warm water through the system. The temperature drop of the water was measured on the differential thermocouples, and the corresponding heat loss was plotted against

difference between mean water temperature and air temperature (Table II; fig. 3).

Table II.—Power Loss from Tubing between Cold Block and Thermocouples.

Difference between mean water temperature and air temperature.	Loss of power.
° C.	Watts.
0·80	0·04
1·20	0·05
1·65	0·05
2·20	0·06
2·95	0·08
3·70	0·11
5·30	0·24
6·00	0·28
7·05	0·28

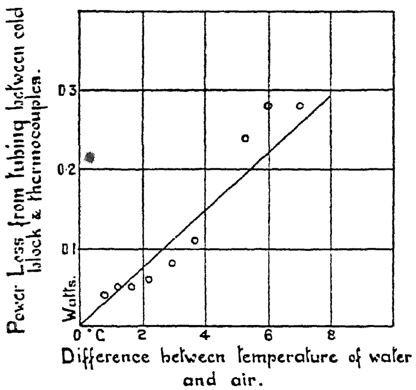


Fig. 3. Power Loss from tubing between cold Block & Thermocouples.

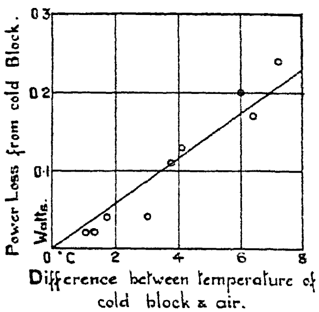


Fig. 4. Power Loss from cold Block.

The spiral round the cold block was then reconnected to the water system and the heat-loss determined once again with warm water flowing. The difference between the two heat losses when corrected for the loss by conduction through the specimen of balsa wood represents the heat loss from the cold block itself. This latter was plotted against the difference between the temperatures of the block and the air (Table III; fig. 4).

Table III.—Power Loss from Cold Block.

Temperature differences between cold block and air.	Total power loss from cold block and tubing.	Power loss from tubing (Fig. 3).	Power loss from cold block.
° C.	Watts.	Watts.	Watts.
1·05	0·06	0·04	0·02
1·30	0·07	0·05	0·02
1·70	0·10	0·06	0·04
3·0	0·16	0·12	0·04
3·75	0·24	0·13	0·11
4·10	0·27	0·14	0·13
6·00	0·39	0·19	0·20
6·4	0·41	0·24	0·17
7·2	0·48	0·24	0·24

This temperature difference was measured by a thermocouple with one junction mounted on the side of the cold block and the other just outside the balsa wood mounting of the cold block.

In figs. 3 and 4 only the parts of the graphs between 0° and 1·5° temperature-excess were actually used; the upper points served, however, to indicate more accurately the true slope of the straight line. The agreement obtained between the power transmitted through the specimen as measured (*a*) by that supplied to the heating grid, and (*b*) by that absorbed by the water, is shown in the last column of Table IV. The mean difference is 1·3 per cent.

(2) *Measurement of Temperature Difference between Hot and Cold Surfaces of Bismuth.*

As already stated, the temperatures of the hot and cold plates were measured by thermocouples pegged in the blocks as near to the surfaces of the plates as possible. The temperatures so measured had to be corrected for (*a*) the temperature drop through the glycerine film at each of the bounding surfaces between the copper and bismuth, and (*b*) any temperature drop in the copper blocks between the couples and the surfaces. The combined correction was determined by placing between the surfaces of the hot and cold blocks a thin piece of copper of thickness 0·005 cms. and using glycerine to make contact. The temperature difference between the hot and cold plates now gave the drop through the two glycerine films above, as the temperature drop through the thin copper was negligible—being equal to 0·0013° C. for a total drop of 0·35° C., *i.e.* only 1 in 300 of the drop through the films. The results are given in Table V. In fig. 5 the temperature drop in the films is plotted against power transmitted.

Table IV.—Comparison of Energy supplied by Heating Coil with that absorbed by Water.

Experiment.	Temperature Measurements.				Power Losses.					Power Measurements.				
	Temperature rise in water.	Inlet temperature.	Mean water temperature.	Air temperature.	Difference between mean water temperature and air temperature.	Power loss from tubing (Fig. 3).	Difference between temperature of cold block and air temperature.	Power loss from cold block (Fig. 4).	Total power loss from cold block and tubing.	Rate of flow of water.	Measured power absorbed by water.	Corrected power reaching cold block.	Corrected power leaving hot block.	Percentage difference between P_w and P_c.
	$\delta\theta$	—	—	—	—	L_1	—	L_2	L_1+L_2	w	$w.\delta\theta.J$	P_w	P_c	—
	° C.	° C.	° C.	° C.	° C.	Watts.	° C.	Watts.	Watts.	c.c./sec.	Watts.	Watts.	Watts.	Per cent.
Glycerine film correction (Table V).	0.322	17.00	17.2	16.7	0.5	0.02	0.8	0.02	0.04	1.300	1.75	1.79	1.84	+2.8
	0.333	17.00	17.2	16.9	0.3	0.01	0.7	0.02	0.03	1.290	1.80	1.83	1.84	+0.5
	0.561	17.55	17.8	17.2	0.6	0.02	0.9	0.03	0.05	1.245	2.93	2.98	3.00	+0.7
	0.397	17.55	17.7	16.9	0.8	0.03	1.3	0.04	0.07	1.320	2.19	2.26	2.25	−0.5
Conductivity of bismuth parallel to trigonal axis (Table VI).	0.341	17.75	17.9	17.8	0.1	0.01	0.5	0.02	0.03	1.215	1.73	1.76	1.78	+1.1
	0.343	18.25	18.4	17.8	0.6	0.02	0.6	0.02	0.04	1.205	1.73	1.77	1.76	−0.6
	0.558	18.35	18.6	17.3	1.3	0.05	1.4	0.04	0.09	1.190	2.79	2.88	2.87	−0.3
	0.574	17.40	17.7	16.9	0.8	0.03	1.1	0.03	0.06	1.190	2.87	2.93	2.88	−1.7
	0.580	16.10	16.4	16.1	0.3	0.01	0.6	0.02	0.03	1.200	2.91	2.94	2.88	−2.1
	0.410	14.90	15.1	14.9	0.2	0.01	0.3	0.01	0.02	1.340	2.30	2.32	2.40	+3.3
	0.410	14.90	15.1	14.8	0.3	0.01	0.4	0.01	0.02	1.350	2.31	2.33	2.39	+2.5
	0.408	14.85	15.1	14.7	0.4	0.01	0.4	0.01	0.02	1.350	2.31	2.33	2.38	+2.1
	0.504	15.55	15.8	15.3	0.5	0.02	0.5	0.02	0.04	1.395	2.94	2.98	3.01	+1.0
	0.502	15.50	15.8	15.6	0.2	0.01	0.6	0.02	0.03	1.400	2.94	2.97	3.00	+1.0
	0.363	15.50	15.7	15.7	0.0	0.00	0.2	0.01	0.01	1.415	2.15	2.16	2.17	+0.5
	0.360	15.55	15.7	15.6	0.1	0.01	0.2	0.01	0.02	1.430	2.16	2.18	2.17	−0.5
Conductivity of bismuth perpendicular to trigonal axis (Table VII).	0.340	15.80	16.0	15.2	0.8	0.03	1.1	0.03	0.06	1.240	1.77	1.83	1.78	−2.8
	0.340	15.90	16.1	15.6	0.5	0.02	0.8	0.02	0.04	1.235	1.76	1.80	1.79	−0.5
	0.570	15.90	16.2	15.9	0.3	0.01	0.8	0.02	0.03	1.215	2.90	2.93	2.93	0.0
	0.571	16.30	16.6	15.8	0.8	0.03	0.5	0.01	0.04	1.210	2.89	2.93	2.91	−0.7
	0.581	16.05	16.4	16.6	−0.2	−0.01	0.3	0.01	0.00	1.185	2.88	2.88	2.93	+1.7
	0.472	14.35	14.6	14.1	0.5	0.02	0.6	0.02	0.04	1.505	2.97	3.01	3.04	+1.0
	0.472	15.05	15.3	15.0	0.3	0.01	0.6	0.02	0.03	1.500	2.96	2.99	3.04	+1.7
	0.507	14.75	15.0	15.1	−0.1	−0.01	0.7	0.02	0.01	1.400	2.97	2.98	3.04	+2.0
	0.510	14.80	15.1	15.1	0.0	0.00	0.7	0.02	0.02	1.400	2.99	3.01	3.04	+1.0

Table V.—Temperature Drop in Glycerine Film.

Hot-plate temperature.	Cold-plate temperature.	Air temperature.	Difference between hot-plate and air temperatures.	Power loss through hot-plate mounting (Fig. 2) (h_1).	Total power supplied to heating grid (h_2).	Power transmitted through glycerine films (h_2-h_1).	Difference between hot-plate and cold-plate temperatures.
° C.	° C.	° C.	° C.	Watts.	Watts.	Watts.	° C.
18·00	17·65	16·70	1·30	0·03	1·87	1·84	0·35
*18·85	18·40	16·85	2·00	0·04	2·29	2·25	0·45
19·20	18·62	17·20	2·00	0·04	3·04	3·00	0·58

* This point was determined after the copper specimen had been removed and replaced, the glycerine films being renewed at the same time.

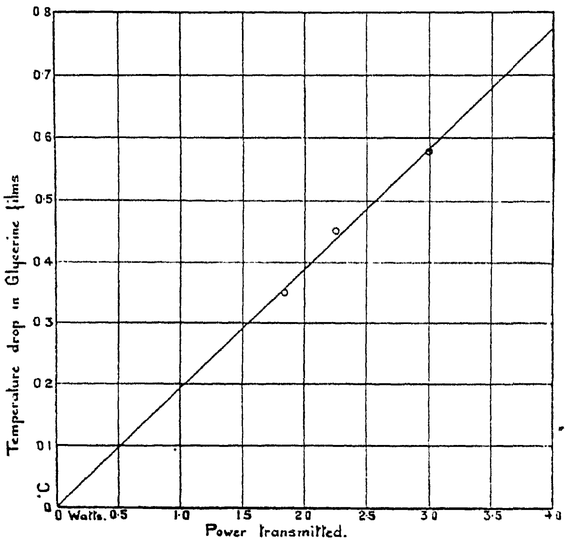


Fig. 5. Temperature drop in Glycerine Film.

(3) *Measurement of Thickness and Area of Specimens.*

The thickness and area of the specimens were measured with an ordinary micrometer gauge.

IV. Results.

The results obtained for the conductivity parallel and perpendicular to the trigonal axis are given in Tables VI and VII respectively. In each case the results are arranged so that each group corresponds to one setting of the specimen. The mean values for each group are given in the last column but

Table VI.—Thermal Conductivity of Bismuth Parallel to Trigonal Axis. Area of Specimen $1 \cdot 023 \times 1 \cdot 842$ sq. cms. $= 1 \cdot 88$ sq. cms.

Thickness of specimen of bismuth.	Temperature Drop.					Power Conducted.					Conductivity.			
	Hot-plate temperature.	Cold-plate temperature.	Difference between hot- and cold-plate temperatures.	Temperature drop in glycerine films.	Temperature drop in specimen.	Air temperature.	Difference between hot-plate and air temperatures.	Loss of power through mounting of hot block.	Power supplied to heating grid.	Power conducted through specimen.	Conductivity.	Mean conductivity for given power.	Mean conductivity of group.	Mean conductivity of thick and thin specimens respectively.
Cms.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	Watts.	Watts.	Watts.	C.g.s.	C.g.s.	C.g.s.	C.g.s.
	21.32	18.58	2.74	0.34	2.40	17.8	3.5	0.07	1.85	1.78	0.0158	0.0156_5	0.0157	
	21.55	18.78	2.77	0.34	2.43	17.8	3.7	0.07	1.83	1.76	0.0155			
	23.85	19.38	4.47	0.56	3.91	17.3	6.5	0.13	3.00	2.87	0.0157	0.0158		
0.168	23.08	18.65	4.43	0.56	3.87	16.9	6.2	0.13	3.01	2.88	0.0159			0.0158_5
	21.64	17.25	4.39	0.56	3.83	16.1	5.5	0.11	2.99	2.88	0.0160		0.0160	
	18.03	15.79	2.24	0.47	1.77	14.9	3.1	0.06	2.46	2.40	0.0158		0.0156	
	18.00	15.74	2.26	0.47	1.79	14.8	3.2	0.07	2.46	2.39	0.0155			
	17.98	15.76	2.22	0.46	1.76	14.7	3.3	0.07	2.45	2.38	0.0156			
0.091	19.35	16.65	2.70	0.58	2.12	15.3	4.0	0.08	3.09	3.01	0.0164			0.0159_7
	19.35	16.65	2.70	0.58	2.12	15.6	3.8	0.08	3.08	3.00	0.0164	0.0164		
	18.28	16.32	1.96	0.42	1.54	15.8	2.4	0.05	2.22	2.17	0.0163		0.0163_5	
	18.30	16.34	1.96	0.42	1.54	15.6	2.7	0.05	2.22	2.17	0.0163	0.0163		

Table VII.—Thermal Conductivity of Bismuth Perpendicular to Trigonal Axis. Area of Specimen $1 \cdot 022 \times 1 \cdot 843 = 1 \cdot 88$ sq. cms.

Thickness of specimen of bismuth.	Temperature Drop.					Power Conducted.					Conductivity.			
	Hot-plate temperature.	Cold-plate temperature.	Difference between hot- and cold-plate temperatures.	Temperature drop in glycerine films.	Temperature drop in specimen.	Air temperature.	Difference between hot-plate and air temperatures.	Loss of power through mounting of hot block.	Power supplied to heating grid.	Power conducted through specimen.	Conductivity.	Mean conductivity for given power.	Mean conductivity of group.	Mean conductivity of thick and thin specimens respectively.
Cms.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	Watts.	Watts.	Watts.	C.g.s.	C.g.s.	C.g.s.	C.g.s.
	18.60	16.55	2.05	0.34	1.71	15.2	3.4	0.07	1.85	1.78	0.0221	0.0221		
	18.47	16.40	2.07	0.35	1.72	15.6	2.9	0.06	1.85	1.79	0.0221		0.0222_5	
0.167	20.32	16.98	3.34	0.57	2.77	15.9	4.4	0.09	3.02	2.93	0.0225	0.0224		
	20.42	17.08	3.34	0.57	2.77	15.8	4.6	0.09	3.00	2.91	0.0223			0.0222
	20.62	17.23	3.39	0.57	2.82	16.6	4.0	0.08	3.01	2.93	0.0221		0.0221	
	17.55	15.38	2.17	0.59	1.58	14.1	3.5	0.07	3.11	3.04	0.0220		0.0218_5	
	18.30	16.11	2.19	0.59	1.60	15.0	3.3	0.07	3.11	3.04	0.0217			
0.0896.. ..	18.31	16.16	2.15	0.59	1.56	15.1	3.2	0.07	3.11	3.04	0.0222			0.0220
	18.31	16.16	2.15	0.59	1.56	15.1	3.2	0.07	3.11	3.04	0.0222		0.0222	

one. They appear to indicate that small variations may arise, probably due to slightly different thicknesses of the glycerine films. The differences are more pronounced in the case of the thin specimens, as would be expected on this explanation. It should be added, however, that varying the pressure from 30 to 60 lbs. per square inch produced no sensible alteration of the results. The numbers in the last column but two indicate that for a given setting of the specimen the result does not depend on the power transmitted, while those in the last column indicate that the result does not depend on the thickness of the specimen.

The following are the mean values at 18° C. :—

Thermal conductivity of bismuth parallel to trigonal axis	= 0·0159 c.g.s.
Thermal conductivity of bismuth perpendicular to trigonal axis	= 0·0221 ,,
Ratio of conductivities	= 1·39

The ratio 1·39 may be compared with that found by other experimenters using the method of measuring the ratio of the axes of the elliptical figure formed by melting a low melting-point coating on the surface of a bismuth crystal. Their values were :—

Lownds*	1·42
Perrot†	1·37
Jaeger‡	1·49

The thermal conductivity of a rod of ordinary bismuth has been determined by Jaeger and Diesselhorst,§ who obtained the value of 0·0193 c.g.s. units at 18° C. This may be compared with the values obtained in the present work by calculating the mean resistance, remembering that resistances and not conductivities are additive, and that the value at right angles to the axis of symmetry must be given double the weight. Thus, if k is the "mean" conductivity,

$$\frac{1}{k}=\frac{1}{3}\left(\frac{1}{0\cdot0159}+\frac{2}{0\cdot0221}\right),$$

therefore

$$k = 0\cdot0195.$$

* Lownds, *loc. cit.*

† Perrot, *loc. cit.*

‡ Jaeger, *loc. cit.*

§ Jaeger and Diesselhorst. 'Sitzung. der Kön. Preuss. Akad.,' pp. 719–26 (1899).

The agreement of this figure with that of Jaeger and Diesselhorst indicates that in the case of bismuth metal in the aggregate, the distribution of the constituent small crystals is random, and that the effect on the thermal conductivity of such inter-crystalline layers as may be present is not appreciable. It is hoped to carry out experiments on other metal crystals to see whether this result is generally true.

V. Summary.

Previously all accurate measurements of the thermal conductivity of metals have been made on bars of heterogeneous structure. It was thought desirable to compare the values so obtained with the more fundamental ones given by single crystals.

A "plate" apparatus has been developed which makes it possible to measure thermal conductivities as high as 0·02 c.g.s. with an accuracy of about 1 per cent., using specimens 2 cms. by 1 cm. in area and about 1 or 2 mm. in thickness.

The thermal conductivities of single crystals of metallic bismuth have been determined in directions parallel and perpendicular to the trigonal axis. The values found at 18° C. were in c.g.s. units :—

Thermal conductivity of bismuth parallel to trigonal axis	= 0·0159
Thermal conductivity of bismuth perpendicular to trigonal axis	= 0·0221
Ratio of conductivities	= 1·39

If a random distribution of crystals is assumed, these figures give a mean conductivity of 0·0195, which agrees well with the value 0·0193 obtained on bars by Jaeger and Diesselhorst in 1899.

We are much indebted to Mr. D. E. A. Jones for his unremitting and careful assistance.

Test of a Theory of Radiation.

By G. P. Thomson, M.A., Fellow of Corpus Christi College, Cambridge, Professor of Natural Philosophy in the University of Aberdeen.

(Communicated by Sir J. J. Thomson, O.M., F.R.S. Received June 5, 1923.)

It is well known that the energy of the electrons ejected from matter by radiation is much greater than could have been given by the radiation to the atom containing the electron on the classical theory of electrodynamics, the discrepancy being especially marked in the case of radiation of high frequency, such as X-rays and γ-rays. To account for this it has sometimes been supposed that the energy in a wave of radiation is not continuously distributed but concentrated in certain small regions. One particular form of this hypothesis has recently been used by Silberstein* in forming a theory of the action of the photographic plate. This regards the energy as concentrated in a few rays, to use the language of geometrical optics, to which Silberstein has given the name of "light darts." It has occurred to the author that the rapid motion of the atoms emitting light in the positive rays affords a means of testing this hypothesis.

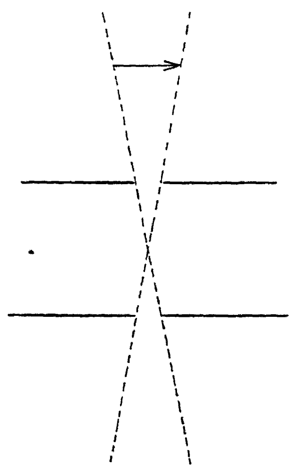


Fig. 1.

Suppose that light from a moving source is made to traverse two slits as in fig. 1. Ignoring diffraction effects, which for the dimensions of the apparatus actually used are inappreciable, only light emitted from that portion of the path of the moving particle which lies between the dotted lines in fig. 1 can get through the slits. If, therefore, the emitting particle is moving so fast that it traverses this portion of its path in less time than it takes to emit a complete "light dart," during some portion at least of the emission the light from the particle will be unable to get through the slit. Thus all the "light darts" will arrive in fragments. Without further elaboration of the hypothesis it would be impossible to say what the effect of these fragmentary "light darts" would be. They might be supposed to act like radiation of proportionally less frequency, or they might be supposed to

* 'Phil. Mag.,' vol. 44, pp. 257, 956.

have no effect until joined by another fragment, but if we are to adhere to the idea of the energy being distributed along the length of the light dart they cannot produce the normal effect of radiation of their own frequency.

Since for light of the wave-length of H_β, for example, any considerable decrease in frequency, such as halving it, would destroy its effect on the eye or an ordinary photographic plate, even for equal energies, it seems reasonable to suppose that if the hypothesis of light darts were true no light could be perceived by these means from particles moving with velocity above a certain limit, determined by the dimensions of the apparatus and the length of the light darts.* In practice certain modifications of this arrangement are required owing to the fact that the light emitted from a beam of positive rays comes partly from atoms of the gas through which the rays are travelling and which are practically at rest (Stark's "ruhende linie"). The arrangement adopted is shown in fig. 2. Light from the positive rays emitted in a direction at

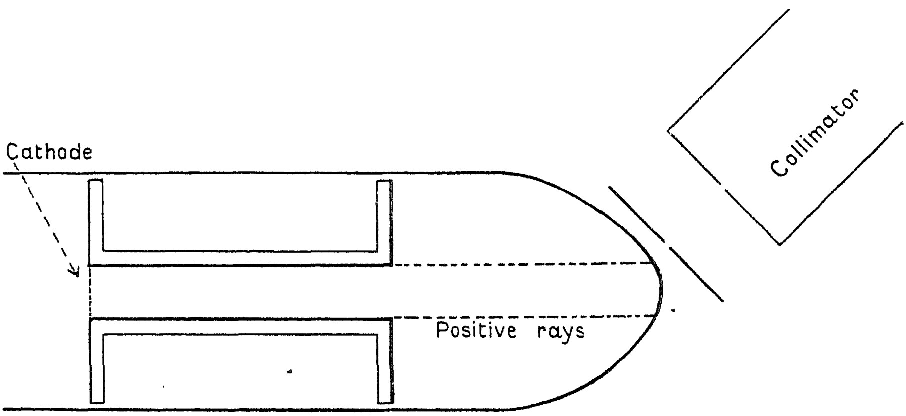


Fig. 2.

45° to that of the motion of the rays passes through the two slits, and is analysed in a spectroscope of sufficient dispersion to show the Doppler effect of the light from the moving atoms. The H_β line thus appears as a broad band of light, or with a fine slit as a sharp line with a diffuse band on the short wave-length side, separated from it by a dark interval. A positive effect would show itself as a diminution in the width of this band owing to the light from the faster moving particles ceasing to be effective. It may be said at once that no such effect was observed.

* The chance of two broken light darts reuniting in an atom to produce an effect can easily be seen to be negligible, except for light of an intensity and duration for which the classical theory would account for the energy effect. The two theories in fact would be experimentally almost indistinguishable.

In order to be certain that the slits used were narrow enough for any conclusions to be drawn, it is necessary to fix a lower limit to the length of the "light darts." Since the various atoms emitting quanta in a source are in no necessary phase relation, interference can only occur over a path difference not greater than the length of the train of waves corresponding to the emission of a quantum, *i.e.*, to the length of a light dart. Unfortunately, the determination of the greatest distance over which interference is possible is complicated in the case of H_β, which is the most suitable line for the experiment, by the fact of its possessing a fine structure. A minimum value can, however, be found from the observed half-width of the components of the line.

If a spectrum is formed having a dispersion of n Ångström per millimetre, and if the distance between the maximum of one of the components of the line and the place where the intensity of that component is half that of the maximum be d, then $d\,n$ is defined as the half-width of the component. Gehreke and Lau* have found for this quantity the value 0·024 Å.U. at the temperature of liquid air. Part, however, of this width is due to the Doppler effect of the thermal agitation of the molecules. Lord Rayleigh† has found an expression for this effect in the form $\frac{\delta\lambda}{\lambda} = 3 \cdot 57 \times 10^{-7}\sqrt{\frac{T}{m}}$, where $\delta\lambda$ is the half-width defined as above, T the absolute temperature, and m the mass of the radiating particle in terms of that of the atom of hydrogen. Since the Balmer series is due to the hydrogen atom $m = 1$ and for H_β, $\delta\lambda = 0 \cdot 017$ at the temperature of liquid air. To find what the half-width of the component would be at the absolute zero we will assume that both the observed lines, and the theoretical widening due to the thermal Doppler effect, show an intensity distribution corresponding to the law of error. While not strictly true for the former (*see* below) the assumption will not involve any serious error. We can therefore combine the effects according to the usual error law and find for the half-width at the absolute zero $\sqrt{(0 \cdot 024^2 - 0 \cdot 017^2)} = 0 \cdot 017$ Å.U.

This width is due to a variety of causes, finite resolving power of the spectroscope used (a Lummer and Gehreke plate), Stark effect on the radiating atoms and, finally, the effect in which we are interested, namely, the finite length of the train of waves emitted without change of phase by each radiating particle. We can find a lower limit for this length by supposing the whole effect due to it, and proceeding as follows. Let L be the required length of the train of waves, then interference cannot occur over a path difference greater

* 'Ann. der Physik,' vol. 67, p. 388.

† 'Phil. Mag.,' vol. 29, p. 276.

than this, and even if the spectroscope were of infinite resolving power, its effective resolving power would correspond to a path difference between the extreme interfering rays and so be finite.

Now the intensity of a line produced by an interference spectroscope of finite resolving power follows the law $\frac{(\sin kx)^2}{kx}$, where x is the distance in millimetres from the maximum and k is a constant depending on the resolving power of the instrument. This law of intensity differs somewhat from the probability law which we have assumed so far, but the difference will not be great if we choose x so that the position where the intensity of the line is half the maximum is the same in the two cases (*i.e.*, $x = d$). Now $\frac{\sin kx}{kx} = \frac{1}{\sqrt{2}}$ when $kx = 1 \cdot 39$ radians, but $nd = nx = 0 \cdot 017$. Hence $\frac{k}{n} = \frac{1 \cdot 39}{0 \cdot 017}$. Again, the first minimum in the line occurs when $kx = \pi$. Hence $nx = \pi \frac{0 \cdot 017}{1 \cdot 39} = 0 \cdot 039$ Å gives the difference in wave-length corresponding to the distance from the centre of the line to the first minimum.

Now, from the theory of the interference spectrometer, to produce a line as narrow as this, would require interference in the spectroscope over N wave-lengths, where $N\lambda = (N - 1)(\lambda + 0 \cdot 039)$, giving $N\lambda = \frac{\lambda^2}{0 \cdot 039}$. But $N\lambda = L$, the distance we require. Hence for H_β, $L = \frac{4861^2}{0 \cdot 039}$ Å $= 6$ cm., and this is the least distance over which the vibrations of a radiator must extend without change of phase for the width of the line to be as little as is actually observed. It gives, therefore, a minimum value for the length of the "light dart."

This supposes that the whole of $0 \cdot 017$Å is due to the finite length of the quanta. Actually part, probably most of it, is due to other causes, the finite resolving power of the spectroscope and the Stark effect in the gas. Indeed there is no reason to suppose the length of a train of waves emitted by a hydrogen atom to be any shorter than those emitted by the atoms of heavy elements, which, as is well known, give interference over distances much greater than 6 cm., 30 or 40 cm. being not unusual. It has, however, been found possible to reduce the length of the wave train used in these experiments to less than 6 cm., so that these arguments from analogy need not be pressed.

As a typical experiment the following figures are given :—

Width of spectroscope slit	0·05 mm.
Width of subsidiary slit	0·033 mm.
Distance between slits	9 mm.
Distance of brightest part of column of light from second slit	5 mm.
Length of path of rays from which light could enter spectroscope	0·08 mm.
Angle between velocity of rays and line of sight ..	45°
Velocity of fastest ray emitting light (from Doppler effect)	$\frac{c}{270}$
Length of longest train of waves which could enter spectroscope from one atom	3·5 cm.

These observations were made visually. Experiments were also made photographically. Here the velocity of the rays was determined by direct measurement of the Doppler effect on the plate. Owing to the faintness of the negatives, even after several hours exposure, they cannot be reproduced, and it was not found possible to work with quite such narrow slits, but here also results were obtained in cases when the train of waves was less than 6 cm.

It should be noticed that more than half of the path of the rays allowed for in this calculation is a sort of "penumbra" from which light could fill only a small proportion of the spectroscope slit. Thus if only light from this portion could be effective in the case of the faster moving molecules, the portion of the spectrum corresponding to these would be greatly reduced in intensity with respect to the rest. As the whole is near the limit of visibility this outer portion would become invisible, causing an apparent diminution in the width of the displaced line. The conditions are thus really considerably more favourable for detecting the effect than would appear from the above calculation, but no effect was observed.

It may, therefore, be safely assumed that the effect does not exist, and that light can be received from a source, and show the usual properties, when the length of the train which can be received from any one emitting particle is less than that emitted without change of phase.

Deductions.

It would seem to follow from this that either :—

(1) Any one emitting particle emits several quanta consecutively in phase with each other. This is contrary to most existing views of radiation.

(2) The energy is concentrated not in lines but at points, one for each quantum emitted.

(3) The energy apparently derived from radiation has really been present all the time in the atoms receiving the radiations, and is released by a trigger effect. As is well known there are grave difficulties attending this view.

(4) The conception of energy does not apply to the phenomena of radiation except statistically.

(5) An electron can collect energy from a wider area than seems possible on the classical theory.

The explanations (2) and (4) seem very difficult to distinguish by direct experiment.

In conclusion I wish to express my sincere thanks to Mr. C. G. Fraser and Mr. A. Macdonald for their assistance in the construction and manipulation of the apparatus used.

Summary.

Experiments are described with positive rays which show that visual and photographic effects can be obtained with trains of waves shorter than those produced in the emission of a quantum of light.

The Ionisation of Nitrogen by Electron Impact.

By H. D. Smyth, Ph.D., National Research Fellow in Physics (U.S.A.).

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received June 20, 1923.)

Introduction.

In a previous paper* the writer suggested a new mode of attack on some ionisation problems and described its application in experiments on mercury vapour. The object of the method is to give a direct means of studying the types of ion produced in a gas or vapour by electrons of known speed. The experimental principle involved is the combination of an ordinary ionising potential apparatus with an arrangement for positive-ray analysis. It does not seem necessary to repeat the general discussion of the advantages to be gained or the difficulties to be overcome in using such a method. Suffice it to say that at first it appeared impossible to deal with substances gaseous at ordinary temperatures, but that now the method has been extended to include them. The nature of the difficulty and the manner in which it can be overcome are best understood by passing directly to the experiments on nitrogen, which are the subject of the present paper.

Method and Preliminary Experiments.

The schematic diagram in fig. 1 represents the general arrangement of electrodes and electric fields in both types of apparatus used for nitrogen.

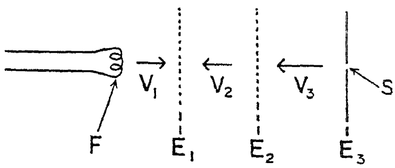


Fig. 1.

Electrons from the filament F are accelerated by the field V_1, and then retarded by V_2 and V_3. The relative magnitudes of the fields are such that few electrons pass beyond E_2 and none reach E_3. On the other hand any positive ions formed between E_1 and E_2 are accelerated by V_2 and V_3 to E_3 where some of them pass through the slit S into the positive-ray analysis chamber. Here they are deflected by a magnetic field and pass through a final slit to an electrode connected to an electrometer. By varying the field V_3 or the

* 'Roy. Soc. Proc.,' A, 102, pp. 283–293 (1922).

magnetic field ions of different m/e are brought on to the detecting plate. Obviously it is essential that the ions should not suffer collision between formation and detection, and herein lies the experimental difficulty.

The first apparatus used for nitrogen was not completely successful and, therefore, will be only very briefly described. In it the electrode E_1 was a disc-shaped grid on a frame of small brass tubing in the centre of a bulb about 5 cm. in diameter. The nitrogen leaked in through four holes in the perimeter of the grid and was carried away by a Langmuir pump through a $\frac{3}{4}$-inch tube opposite the edge of the grid. In this way it was hoped that the molecular density would be sufficient at E_1 for the production of ions, but too small in other parts of the apparatus to scatter these ions before they were detected in the positive-ray box. The positive-ray arrangement was the one used for mercury with minor alterations. The general experimental procedure was also the same as for mercury.

Early observations with this apparatus were encouraging, but failed to give as definite results as were desired. The stray effects from scattering, filament gas, hydrocarbons from wax joints, etc., were so great that it was impossible to be certain of the effects due to nitrogen, except when they were very large. This remained true even when measurements had continued for some time, and a large number of curves were available for comparison. The only conclusions that could be drawn were that the ordinary ionising potential of nitrogen at about 17 volts corresponds to the production of singly charged molecular ions, and that atomic ions are not produced till somewhere in the neighbourhood of 30 volts. Though a number of curves showed peaks which seemed due to doubly charged atomic ions, it was not possible to determine the conditions necessary for their formation.

Final Apparatus and Procedure.

The second apparatus is shown in fig. 2, which is drawn to scale except for the exaggeration of the slit S_2. The essential improvement is that the ionisation chamber, *i.e.*, the region between the electrodes E_1 and E_2, is shut off from the region where the positive ions are accelerated by the platinum foil electrode E_2 which has only the small slit S_1 enabling a beam of positive ions to pass through it. Gas from an artificial leak enters at A and is pumped out chiefly through the large side-tube B, connecting to a Langmuir pump. A small amount of gas diffuses into the positive-ray box through the slit S_2 of width 0·5 mm., but is exhausted by a second Langmuir pump working through C and D and using the high vacuum of the first pump as fore vacuum. Thus,

though there may be a fair pressure of gas in the ionisation chamber, it will be much smaller between S_1 and S_2 and still less beyond S_2. In this way,

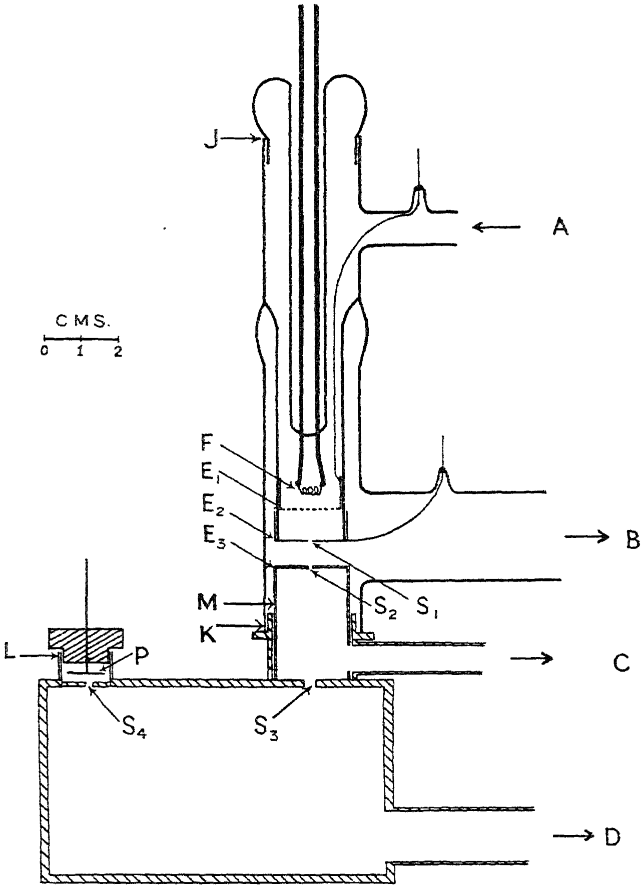


Fig. 2.

scattering by nitrogen is reduced to a minimum, but there remain other stray effects to guard against. For this purpose liquid air is kept on traps in the intake tube A as well as in the exhausting tubes B, C, and D. This prevents mercury vapour or vapour from tap grease getting into the apparatus. There remains, however, sealing-wax vapour from the joints J, K, L, etc., and gas occluded in the tungsten filament, platinum electrodes and glass walls. On account of the proximity of K to the ionisation chamber it is not possible to bake out properly. The unfortunate consequences of this fact will be discussed in connection with the experimental results.

Before leaving the subject of gas and pumps it may be well to point out that it is impossible to know what the gas pressure is in the ionisation chamber.

The procedure is to read the pressure on a McLeod gauge some distance along B, then shut off the pumps for one minute and read it again. This gives an arbitrary standard for the artificial leak and allows conditions to be reproduced, but, of course, gives only a rough idea of the pressure near E_1. The readings taken in this way on nitrogen were of the order of $p = 0 \cdot 0006$ mm. with the pumps running, increasing to $p = 0 \cdot 0030$ in one minute with the pumps shut off. The pressure in the ionisation chamber, therefore, was probably in the neighbourhood of $0 \cdot 001$ mm.

Nitrogen was prepared by the reaction of bromine and ammonia as described by Waran.* It was stored over phosphorus pentoxide.

Turning now to the positive-ray apparatus, an important improvement was made by the introduction of a powerful electro-magnet giving a field up to 4000 or 5000 gauss, with pole pieces 9 cm. by 10 cm. in cross-section and $2 \cdot 9$ cm. apart. Correspondingly, a new positive-ray box, shown in fig. 2, was made, in which the ions are bent in a semicircle in order to reach the detecting plate P, back of the slit S_4. This gives a focussing effect and makes it possible to have S_3 large, thus somewhat compensating the effect of the small width of S_2 in reducing the intensity. The positive-ray box is of $\frac{1}{8}$-inch brass, with the iron cylinder M extending into the ionisation tube as before. The plate P is of brass insulated by an ebonite plug.

The effect of the stray field of this powerful magnet was found so great that a compensating electromagnet had to be introduced, with its poles just outside the ionisation chamber. The thermionic current to E_1 is unaffected by the magnetic fields, but if V_2 is reversed and the thermionic current to E_2 measured it is found to be very sensitive to changes in the magnet currents. The compensating magnet, therefore, was calibrated for various currents in the big magnet by finding the setting which gave the maximum thermionic current to E_2. When an ionisation experiment is in progress there is no check on the degree of compensation of the fields.

The difficulty discussed in the last paragraph led to an important change of procedure. Instead of setting all the electric fields and then observing the variation of the electrometer current as the magnetic field is varied, the present procedure is to set the magnetic field and the electric fields V_1 and V_2, and then observe the electrometer current for different values of the field V_3. This current is then plotted against $\frac{1}{V_2 + V_3}$ which is proportional to the m/e of the ions if they are produced just at the electrode E_1.

* H. P. Waran, 'Phil. Mag.,' vol. 42, p. 246 (1921).

The electrodes are kept at the potentials desired by a cabinet of small cells giving up to a thousand volts. The scheme of connections differs somewhat according to the magnitude of V_1. At values below 40 volts V_1 and V_2 are kept equal, while at higher values it is found convenient to keep $V_2 = 40$ volts, irrespective of the value of V_1. This means that electrons reach E_2 with a high velocity, but even the small fraction that pass through S_1 come quickly into the uncompensated stray field and are deflected away from the path of the positive ions. By this scheme most of the ionising collisions take place with speeds of the impacting electrons varying over a range of only forty volts. The values of V_1 at low voltages are read on a Weston voltmeter of 30 volts and 150 volt scales, which has been checked against a standard instrument. For values of V_1 above 150 and for all values of V_2 and V_3 the voltages are assumed from the number of cells, but checked occasionally with an electrostatic voltmeter. V_3 can be varied in steps of two volts. The current, i, to E_1 is read on a Weston microammeter and is of the order of 100 to 1000 microamperes. The potential drop across the filament is between 3 and 4 volts and connections are made so that this correction to V_1 is of the opposite sign to that due to the initial velocity of the electrons.

Since positive ions may originate anywhere between E_1 and E_2 they may reach S_1 with any velocities between V_1 and zero. Therefore it is desirable to have V_3 large compared to V_2, so that the positive-ray beam defined by S_2 may be as homogeneous as possible. Unfortunately, the unexpectedly large stray field of the magnet makes it desirable to work with small magnetic fields and correspondingly small values of V_3. For the molecular ion of nitrogen $m/e = 28$, the value of V_3 used was from 80 to 120 volts. This accounts for the comparatively great width of this peak in the curves which will now be presented.

Results.

A typical curve is shown in fig. 3, where the ordinates are given in terms of m/e on the scale $m/e = 1$ for atomic hydrogen. To obtain this scale from the values of $\frac{1}{V_2 + V_3}$ against which the curve was originally plotted, it was necessary to assume the peak $m/e = 14$, and by taking its average position over a number of curves determine a scale of m/e for a given magnetic field. As a check on this, the value of m/e was calculated for this peak from the known value of the magnetic field and found to be 15, an agreement well within the limits of error of the method. All the curves presented were taken with a field of 3050 gauss.

Besides this peak at 14 attributed to a singly charged atomic nitrogen there are three other maxima in the curve. The very large one at about 27 is attri-

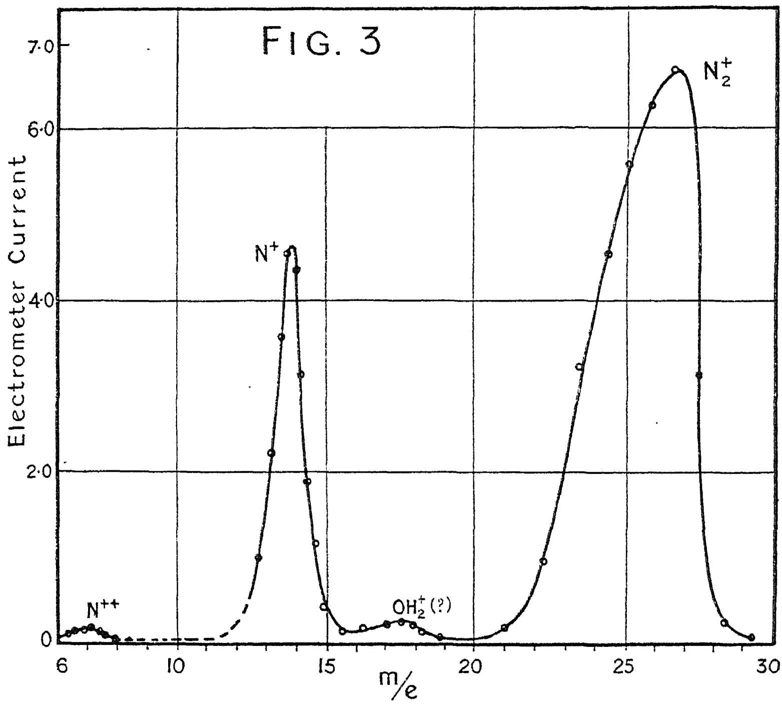


FIG. 3.—V_1 = 100 volts; V_2 = 40 volts.

buted to singly charged molecular nitrogen. As has been mentioned before the reason for its great width and its somewhat low value of m/e is the comparatively small value of V_3. Measured in volts, the width of all three nitrogen peaks at half-value is about 20. Of the two small minima, the one at 7 is due to doubly charged atomic nitrogen, while that at 17·5 is an impurity.

As this last was never entirely eliminated, it may be well to discuss it before anything more is said about the nitrogen. At first, it was thought to be NH_3^+ carried over from the nitrogen generator, but it was soon found that it originated in the ionisation chamber. If the artificial leak was shut off, the other three peaks disappeared, while that between 17 and 18 increased in intensity. Moreover, in a run taken just after a new filament had been put in, the impurity peak was as great as that due to molecular nitrogen. Further, by putting a cooling system on the wax joint K it was possible to bake out the ionisation chamber at a temperature of 220°. Both this and prolonged bombardment of the electrodes very markedly reduced the intensity of the impurity.

All this evidence indicates that the effect was due to water vapour occluded in the tube. Whether the ions were present as OH^+ or OH_2^+ is not certain. In several curves there seemed to be two peaks, but in most there was a fairly sharp single peak whose average position in twelve runs was $m/e = 17 \cdot 75$, with an average deviation of $0 \cdot 13$. Thus it is probable that the OH_2^+ ion predominated. A single determination of its ionising potential gave $14 \cdot 1 \pm 1 \cdot 0$ volts.

However, for our present purposes, the chief question about this impurity is its effect on the behaviour of the nitrogen peaks. Not the slightest correlation was detected between the intensity of the water-vapour peak and that of any

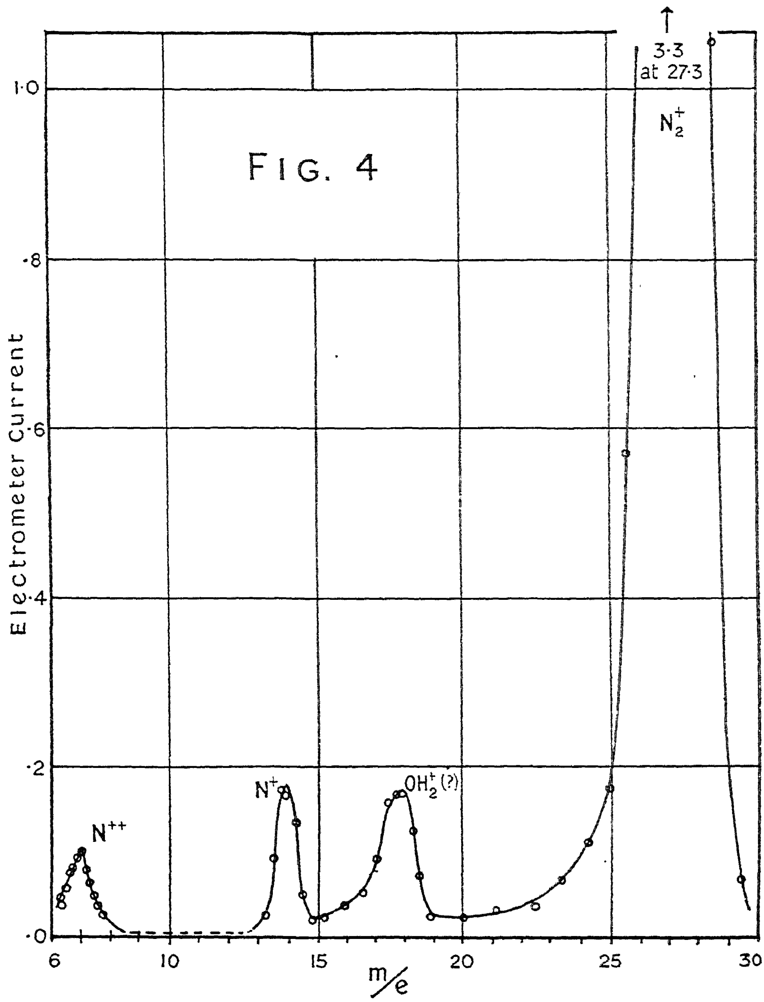
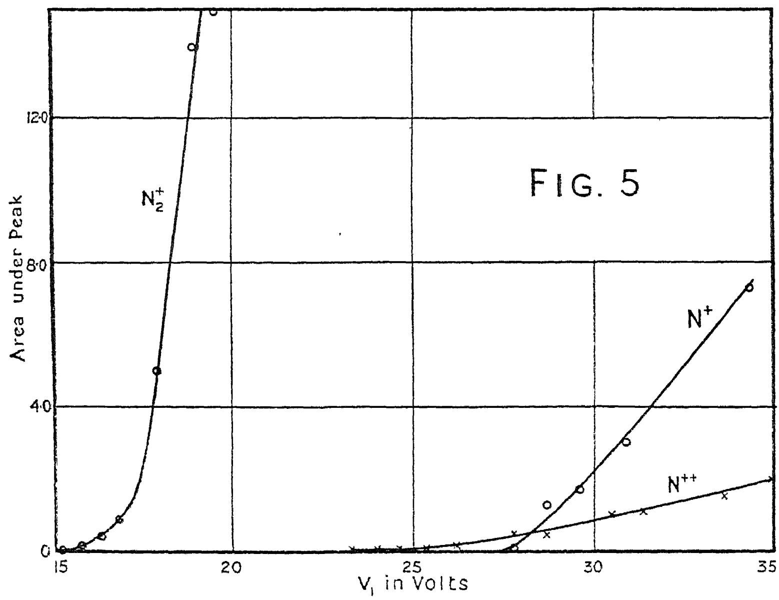


FIG. 4.—$V_1 = 30$ volts ; $V_2 = 30$ volts.

of the nitrogen peaks. For example, the curve shown in fig. 3 and the one mentioned above, where the water-vapour peak was so large, were taken under the same voltage conditions and are entirely alike in regard to the nitrogen peaks.

As to other possible impurities, there were no other peaks detected between $m/e = 3$ and $m/e = 35$, and outside of this range the only impurity likely to be present in considerable quantity was hydrogen. One might expect the amount of hydrogen present to vary in about the same way as water vapour and therefore can apply the same remarks to it. Let us turn then to the results on nitrogen in the belief that they really represent its behaviour independent of impurities.

A comparison of fig. 3 and fig. 4 shows that the most striking change caused by the reduction of V_1 from 100 to 30 is in the relative intensity of N^+. If the voltage is further reduced to 27, the N^+ peak is hardly detectable, though the N^{++} peak is still quite strong and $N_2{}^+$ is enormous. At about 24 volts the N^{++} peak disappears while the $N_2{}^+$ peak persists to about 17 volts. It is difficult to determine these points exactly, as the peak simply flattens out and becomes merged in the stray effect. The curves in fig. 5 represent the



areas under the three types of peak plotted against V_1. In this particular series the $N_2{}^+$ persisted to about 15·5 though the other two peaks disappeared at the usual values. To determine the absolute value of the critical potentials,

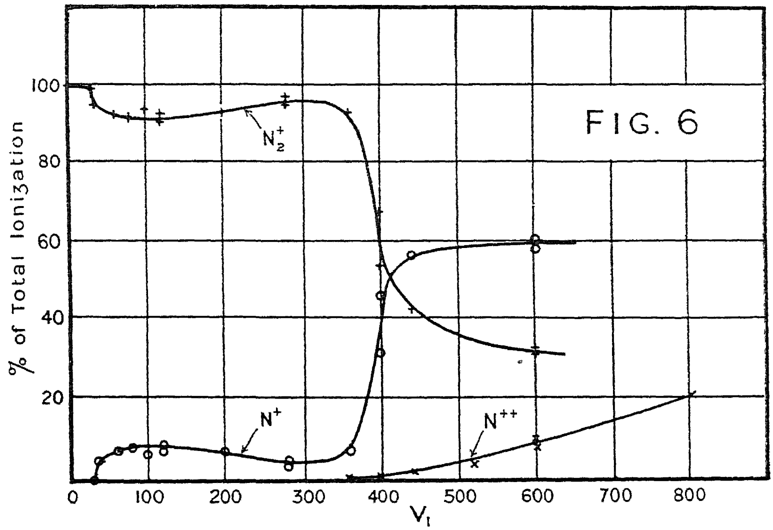
that for N_2^+ was assumed 16·9 from the work of Foote and Mohler,* and of Brandt† (as corrected by Franck‡). In this way a correction to the observed voltage is determined. The final values are given in the following table :—

Table I.—Experimental Results.

Type of Ion.	Critical Potential.	Computed Error.	Estimated Error.	Remarks.
N_2^+	16·9			Assumed.
N^{-+}	24·1	$\pm 0·62$	$\pm 1·0$	Brandt found increased ionisation at $24·7 \pm 0·1$ and $30·0 \pm 0·2$.
N^-	27·7	$\pm 0·07$	$\pm 0·8$	
H_2O^+(?)	(14·1)		$(\pm 1·5)$	

where the values given are the weighted means of values obtained from different sets of observations. As the computed probable error takes no account of errors in weighting, estimates of the real probable error have been added.

So much for the voltages at which the different ions are first detectable ;



let us now consider their variation in relative intensity as V_1 is increased. This is shown by the curves in fig. 6, where the percentage of the total effect

* Foote and Mohler, 'The Origin of Spectra,' p. 66 (1922).

† E. Brandt, 'Zs. f. Phys.,' vol. 8, pp. 32–44 (1921).

‡ J. Franck, 'Zs. f. Phys.,' vol. 11, p. 160 (1922).

due to each type of ion is plotted against V_1. No great value should be attached to the numerical values, as it was found that the slight alteration caused by the replacement of a filament changed the relative intensities at a given voltage very materially. However, it did not alter the general shape of the curves, and it is this which is of chief interest. For voltages below a hundred it is seen that the relative intensity of N^+ increases steadily. In fact, within the limits of error, it is an hyperbolic function of V_1. However, instead of continuing to increase or of approaching a limit, it begins a gradual decrease, reaching a minimum at about 300 volts. Some 50 volts beyond this point a sharp increase takes place, bringing it up to nearly 60 per cent. of the total at 450 volts. From here on to 600 the relative intensity of N^+ remains practically constant. Since the intensity of N^{++} is negligible up to 400 the curve for N_2^+ is simply the complement of that for N^+. It is interesting to note that simultaneously with the change in proportions of N^+ and N_2^+ the relative intensity of N^{++} begins to increase markedly. Another group of runs showed the sharp rise in the proportion of N^+ present occurring between 320 and 360, so that these experiments cannot be regarded as fixing this point very definitely.

So far we have discussed the variation of intensities with V_1; experiments were also made on the effect of varying the thermionic current. The voltage V_1 was set at 35, and each peak measured with a very high current, then with about a quarter the current, and then with it high again. The ratios of the intensities per unit current at high currents to those at low were found to be 0·88, 0·8 and 0·83 for the N^{++}, N^+ and N_2^+ peaks respectively. This indicates an intensity rising at less than the first power of the current to E_1 and in the same way for all three types of ion. The conclusion is that they were all produced by single impacts.

In order to supplement all these results on positive ions, an attempt was made to study the formation of negative ions. In spite of the unfavourable arrangement of fields necessary quite a sharp peak was obtained for N_2^-. However, its intensity was very small even with very large thermionic currents, and it was not possible to be certain of anything more than its existence. A minute trace of a negative ion at about $m/e = 16$ was also found, probably OH^-, but so slight as to make even its identity doubtful. No trace of any other negative ions was observed.

Discussion of Results.

Let us now consider the bearing of these results on previous experiments and theories. Several years ago Davis and Goucher* found two excitation potentials in nitrogen, and a little later the writer† found three at 8·29, 7·3(?) and 6·29. The first two values seemed to fit certain doublets found by Lyman in the Schumann region, but the third value was provisionally attributed to the production of the band spectrum. By a very careful and detailed piece of experimental work, Brandt‡ found a whole series of excitation potentials between 7·2 and 8·5 volts, and concluded that they correspond to the production of bands in the extreme ultra-violet. This is entirely supported by the present work as well as by recent spectroscopic evidence. It remains a very curious fact that the strongest excitation potential coincides with the nitrogen doublet 1492·8, 1494·8, although there is every reason to suppose little or no atomic nitrogen present. Possibly a fuller knowledge of the relation between the electron transitions in the atom and molecule may explain it.

As to the ordinary first ionising potential at 16·9 volts, it is now definitely proved to be the ionisation of the molecule without dissociation and, therefore, should be correlated with the band spectrum. Unfortunately our knowledge of the band spectrum is too limited to give a satisfactory calculation of the ionising potential. However, by introducing some rather questionable assumptions, a calculation can be made, and a value of 17·6 volts is obtained. The writer hopes to discuss this question in another paper.

Though no quantitative comparison with chemical models is possible, the high value of the ionising potential, comparable with those of the rare gases, corresponds to the chemical inactivity of nitrogen, and the production of molecular rather than atomic ions to a high heat of dissociation, indicating great stability of the molecule.

The most remarkable point to be explained is the production of doubly charged atomic ions at lower voltages than singly charged. One is tempted to suppose that at 24·1 volts most electrons simply produce a molecular ion, but that on rare occasions the collision results in a doubly charged atom and a neutral or even negatively charged atom. Then at 27·7 volts it becomes possible for an electron to split the molecule into two positively charged atoms, though the other two types of collision are still possible also. These suggestions are embodied in Table II.

* Bergen Davis and F. S. Goucher, 'Phys. Rev.,' vol. 13, pp. 1–5 (1919).

† 'Phys. Rev.,' vol. 14, pp. 409–426 (1919).

‡ E. Brandt, *op. cit.*

Table II.

Critical Potential.	Probable Reaction.	Energy Equation.
16·9	$N_2 \rightarrow N_2{}^+$	$16\cdot9 = J$ .... (1)
24·1	$\begin{cases} N_2 \rightarrow N^{++} + N \\ N_2 \rightarrow N^{++} + N^- \end{cases}$	$24\cdot1 = D + J''$ .... (2*a*) $24\cdot1 = D + J'' - E$ .... (2*b*)
27·7	$N_2 \rightarrow N^+ + N^+$	$27\cdot7 = D + 2J'$ .... (3)

where

J = Ionising potential of molecule.

J' = First ionising potential of atom.

J'' = Second ionising potential of atom.

D = Heat of dissociation of molecule.

E = Electron affinity of atom.

If we assume that D is of the order of 6 volts (138,000 calories) and E of the order of one volt, we get from (3) $J' = 11$ volts roughly and from (2*a*) $J'' = 18$ or, from (2*b*) $J'' = 19$. It is evident, therefore, that the explanations offered satisfy the energy relations and give reasonable values for the ionising potentials of atomic nitrogen. The results on negative ions though not conclusive were unfavourable to reaction (2*b*).

One further complication that may arise is the production of doubly charged molecular ions $N_2{}^{++}$. These would not be distinguishable from the N^+ ions which so far have been assumed as the cause of the peak at $m/e = 14$. In general, Sir J. J. Thomson* finds the occurrence of multiply charged molecules very rare, but does find a trace of a doubly charged molecule, due either to nitrogen or carbon monoxide. Nevertheless, it seems highly improbable that the large effects observed are due to the production of $N_2{}^+$. Such an explanation would make it almost impossible to account for the presence of N^{++} at such low voltages. Still it would be very interesting to try some method which would separate ions of the same m/e but of different charge.

When the voltage V_1 is increased to about 70 volts and $V_2 = 40$, all the primary collisions of electrons with molecules between E_1 and E_2 may result in any one of the three reactions. The probability of producing any one of them will presumably depend not only on the energy required but also on the

* J. J. Thomson, 'Rays of Positive Electricity,' 2nd edn., p. 84 (1921).

time of collision. In the cases where ionisation is accompanied by dissociation more time may be required than for the simple expulsion of an electron. Thus at first the relative intensities of the atomic peaks would increase until all electron impacts were of more than the minimum energy required. Then the speed factor would become dominant and their relative intensity might fall off again. This in a rough way seems to explain the curves in fig. 6 up to 300 volts.

Now the K-limit for nitrogen according to Foote and Mohler* is 375 volts, and, therefore, a sudden change in the probability of dissociation might well be expected when the impacting electrons attain this speed. Thus between 350 and 450 volts the proportion of atomic ions increases rapidly, as shown in fig. 6. Moreover, once the K-ring is penetrated, the disruption of the molecule will be much more violent, and it is natural to expect an increase in the proportion of doubly charged ions. This effect will be aided also by the enormous increase of photo-electric ionisation.

It is hoped that as the experiments on other gases are continued the results at high voltages can be made more precise and enough material accumulated to throw some light on the mechanism of ionisation as well as molecular structure. Experiments on hydrogen are in progress.

Summary.

1. The method of studying ionising potentials previously used for mercury has been improved and extended to gases.

2. Results on nitrogen show that the ordinary ionising potential at 16·9 volts corresponds to the production of singly charged molecular ions, that doubly charged atomic ions appear at $24 \cdot 1 \pm 1 \cdot 0$ volts and singly charged atomic ions at $27 \cdot 7 \pm 0 \cdot 8$ volts.

3. These results are explained as corresponding to the transitions $N_2 \rightarrow N_2{}^+$, $N_2 \rightarrow N^{++} + N$ (or N^-) and $N_2 \rightarrow N^+ + N^+$. This leads to values of 11 and 18 volts for the first and second ionising potentials of atomic nitrogen.

4. Further results at higher voltages show the variation of the relative intensity of the different types of ion with voltage. In particular, there is a very sharp increase in the proportion of atomic ions between 350 and 400 volts, corresponding roughly to the K-limit of 375 volts found by Foote and Mohler.

* Foote and Mohler, 'The Origin of Spectra,' p. 195 (1922).

5. It was found possible to produce negatively charged molecular ions but only in very small quantities. No atomic negative ions were observed.

In conclusion, it gives the writer great pleasure to express his gratitude to Sir Ernest Rutherford for his continued interest and the privileges of the Laboratory. The continuance of this work has been made possible by a Fellowship from the National Research Council.

The Catalytic Decomposition of Sodium Hypochlorite by Cobalt Peroxide.

By Owen Rhys Howell.

(Communicated by Prof. T. M. Lowry, F.R.S. Received April 10, 1923.)

There are frequent references in the literature to the decomposition of hypochlorite solutions on keeping or by heating, and to their decomposition by light.

The first mention of their decomposition by metallic oxides is by Balard (1) who observed that in the presence of silver oxide hypochlorites are decomposed with evolution of oxygen. Gay Lussac (2) found a similar decomposition in the presence of powdered pyrolusite, and this was confirmed by Mitscherlich (3). Fleitmann (4) suggested warming hypochlorite solutions with the oxides of cobalt, nickel, copper or iron as a means of preparing oxygen, and Bidet (5) described a method of obtaining a continuous stream of oxygen by the action of cobalt oxide on bleaching powder. Böttger (6) has examined the action of barium peroxide.

Several references occur to the rapidity of decomposition of bleach liquors containing iron (7) or copper (8), or in contact with metals (9) and the relative effects of various metallic oxides have also been examined (10).

No quantitative examination of the decompositon by metallic peroxides appears to have been made. During an investigation (11) of the precipitation of the higher oxide of cobalt by means of alkali and hypochlorite, interest was aroused in the decomposition of the excess of hypochlorite by the precipitated oxide and this reaction has now been investigated.

Materials.—The sodium hypochlorite solution was made by bubbling washed chlorine, generated from potassium permanganate and hydrochloric acid, into aqueous sodium hydroxide below 15°. A little free alkali was left to retard

decomposition of the hypochlorite. The hypochlorite was determined by adding the solution to potassium iodide acidified with hydrochloric acid and titrating the liberated iodine against sodium thiosulphate; the alkali by adding neutralised hydrogen peroxide to remove the hypochlorite and titrating against acid.

The cobalt peroxide was made by precipitating cobalt sulphate, free from iron and nickel, with sodium hydroxide and sodium hypochlorite. One and a half equivalents of alkali and one equivalent of hypochlorite were used. After decomposition of the excess of hypochlorite was complete, another equivalent was added, and after decomposition of this a further half equivalent. In this way a fully oxidised precipitate was obtained (11). The precipitate was allowed to settle and washed by decantation three times, after which it remained too long in suspension for further similar treatment. It was filtered and washed on a Buchner funnel until the filtrate was almost free from alkali. It was then shaken up with water and stored for about 3 months before use. The suspension, decanted from the small amount of sediment, was 0·033 molar and was very stable.

Apparatus.—The reaction vessel is shown in fig. 1. It consisted of a large boiling-tube T fitted with a rubber stopper. The stirrer was of glass rod bent in the form shown and was extremely efficient. The importance of effective agitation in reactions involving the evolution of gas has been pointed out by Lamplough (12), and especially in the presence of colloids by Findlay (13). This particular reaction is a worthy illustration; a solution of a hypochlorite remains in contact with cobalt peroxide with practically no evolution of gas for a considerable period, but when stirred it evolves oxygen continuously. With a stirring speed of 1600 revolutions per minute strictly comparable results were obtained.

The stirrer worked through a mercury seal. Attention may be called to some features of this. Usually a tube is fitted to the stirrer inside A, to rotate resting on the guide-tube B. This is in general unsatisfactory, for the whole weight of the stirrer is borne by this glass—glass bearing, which is rapidly worn away and often seizes with a mixture of glass dust and lubricant. In the arrangement sketched, this tube is dispensed with, and instead a guide tube C is used immediately beneath the pulley. A suitable washer may be introduced between. This device has the advantage of being easily lubricated and readily adjusted to bring the stirrer to the necessary height. The tube A is made fairly long, and not only fixed to the stirrer by a rubber stopper but kept concentric with it by means of a piece of rubber tubing D. The stirrer and tube then run together quite evenly without any "wobble." In order to prevent any lubricant running down the stirrer from the bearing a

little trap E, consisting of a small piece of glass tubing, was fixed to the stirrer by a rubber stopper. A side tube S, entering tangentially, closed

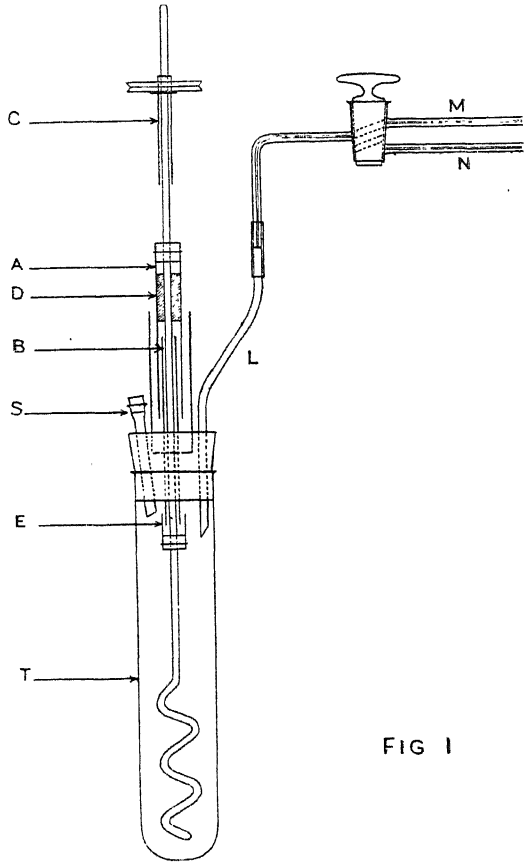


FIG I

by a rubber stopper, was used for introducing one of the reactants by means of a pipette.

The reaction vessel was immersed up to the stopper in a thermostat kept at the necessary temperature. In all cases, except in the series for determination of the temperature coefficient, this was 40° C. The gas supply was led to the regulator through a governor, reducing the pressure to $2\frac{1}{4}$ inches of water, and a film of high-boiling paraffin was kept on the surface of the water in the thermostat to prevent evaporation. In this way the temperature was maintained constant to within $\pm 0{\cdot}01°$.

The gas evolved escaped through the tube L, which was joined to a three-way tap. One arm, M, was open to atmosphere and the other, N, connected to the gas burette. The burette, together with a tube of about the same bore

open at the top to atmosphere, was jacketted in a wide tube filled with water. At their lower ends the burette and open tube were joined and connected to a levelling tube, the arrangement being filled with water. As evolution of gas proceeded the levelling tube was lowered so that the water in the burette and open tube were at the same level, the gas thus being at atmospheric pressure.

Method of Experiment.—The amount of hypochlorite solution taken was sufficient to yield about 75 c.c. of oxygen. The requisite quantity of hypochlorite solution and of alkali or sodium chloride were made up to 100 c.c., and 60 c.c. of this pipetted into the reaction vessel. This was allowed to remain slowly stirred in the thermostat for half an hour to attain the requisite temperature. 10 c.c. of the cobalt peroxide suspension, which had been standing for the same time in the thermostat, were then run in and connection was made with the gas burette. The stirrer was set in rapid rotation and a stop-watch started at the same instant. Although this gave very nearly the true starting point of the reaction, a small correction (amounting to not more than about 0·2 minute), computed from the gas volumes, was applied in some cases.

Volume readings were taken every minute for the first hour, every 10 minutes for the second hour, every 20 minutes for the third hour, and then at intervals until there was no further change in volume. The reaction in some cases took as much as 9 hours to complete. The final volume of gas agreed closely with that calculated from the hypochlorite taken. All the readings taken were reduced to N.T.P.

The velocity of the reaction was calculated from the expression for a monomolecular reaction—

$$k = \frac{2{\cdot}30}{t}\left(\log_{10} V_\infty - \log_{10}(V_\infty - V_t)\right)$$

the unit of time being the minute. It was found that the velocity coefficient increases in value as the reaction proceeds. In order to obtain strictly comparable results, the fraction, F, of the hypochlorite decomposed was also calculated for the corresponding values of k.

Effect of the Catalyst.

It was found that using solutions of the same composition with the same volume of cobalt peroxide suspension for decomposition, perfectly reproducible values could be obtained for the velocity coefficient, the agreement being within one-half of 1 per cent.

A series of experiments was made, using a solution of the same concentration in each case with varying amounts of catalyst. The concentration of

the solution after addition of the catalyst at the beginning of the reaction was in all cases as follows :—

NaOCl, 1·14 M ; NaCl, 1·14 M ; NaOH, 0·28 N ; Na_2CO_3, 0·16 N ;

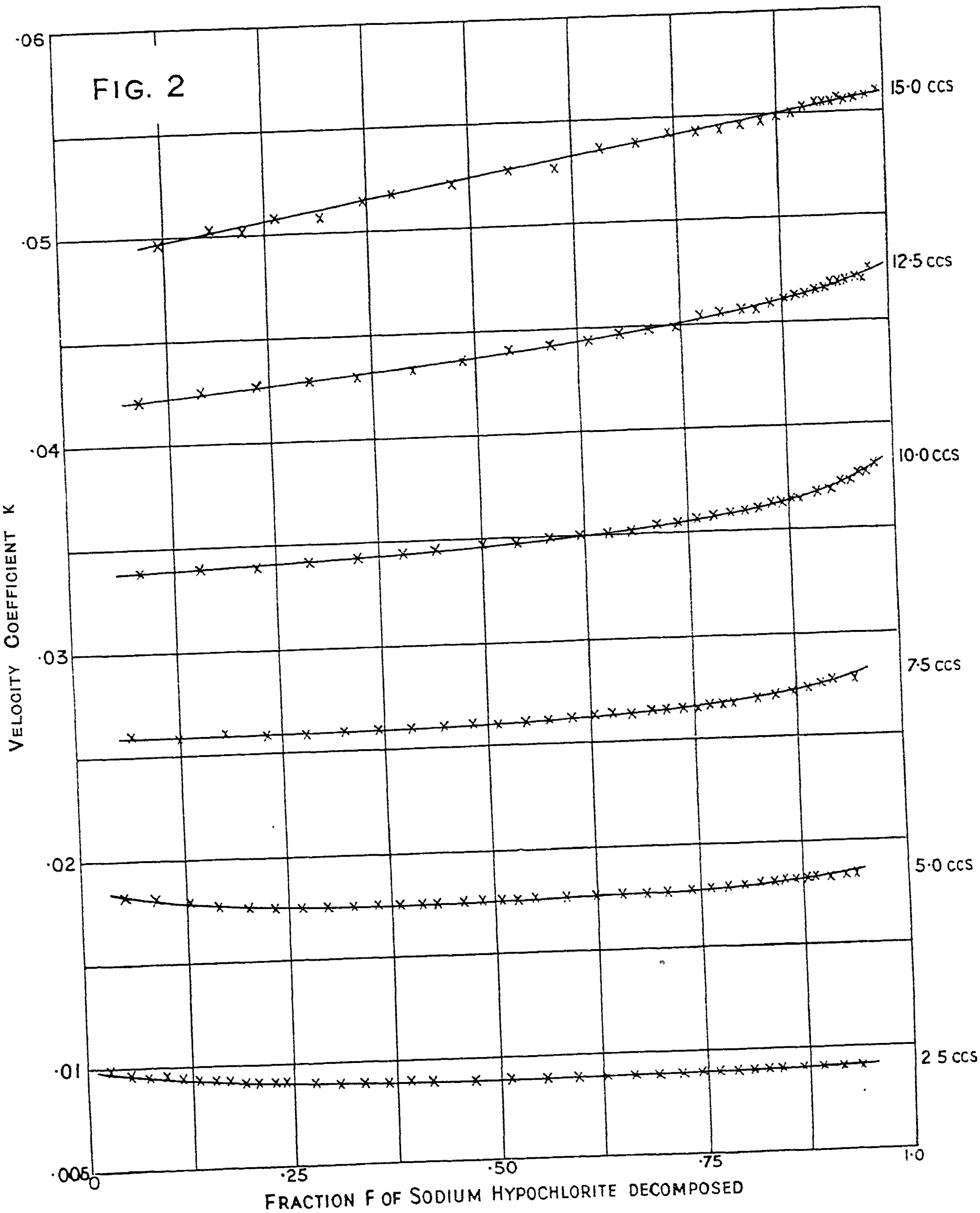
and the amount of catalyst present varied from 2·5 to 15 c.c.

The type of results obtained at various rates is shown by Table I, where details of two experiments are given in full, and by fig. 2, where the whole series is plotted. It is seen that the reaction proceeds more rapidly as decomposition proceeds, and that the increase is more marked the more rapid the rate. This increase is fully accounted for by the acceleration produced by relative increasing concentration of sodium ions compared with the diminishing concentration of sodium hypochlorite (see below). The small initial decrease

Table I.

2·5 c.c. of catalyst.		5·0 c.c. of catalyst.	
F.	*k*.	F.	*k*.
0·026	0·00985	0·046	0·01820
0·048	0·00961	0·086	0·01803
0·070	0·00952	0·126	0·01794
0·092	0·00959	0·162	0·01769
0·112	0·00941	0·198	0·01764
0·132	0·00934	0·231	0·01750
0·151	0·00929	0·264	0·01750
0·169	0·00925	0·296	0.01753
0·187	0·00913	0·326	0·01750
0·205	0·00911	0·356	0·01759
0·223	0·00909	0.384	0·01757
0·239	0·00906	0·410	0·01757
0·272	0·00902	0·429	0·01754
0·302	0·00897	0·461	0·01762
0·333	0·00897	0·484	0·01762
0·362	0·00897	0·507	0·01766
0·389	0·00895	0·527	0·01762
0·416	0·00895	0·548	0·01762
0·466	0·00895	0·586	0·01764
0·511	0·00895	0·622	0·01766
0·555	0·00897	0·654	0·01768
0·593	0·00897	0·684	0·01768
0·629	0·00899	0·711	0·01773
0·661	0·00899	0·738	0·01782
0·690	0·00899	0·761	0·01787
0·717	0·00899	0·783	0·01792
0·743	0·00904	0·802	0·01798
0·763	0·00899	0·820	0·01803
0·785	0·00902	0·837	0·01810
0·804	0·00902	0·852	0·01817
0·822	0·00906	0·865	0·01819
0·838	0·00906	0·877	0·01821
0·866	0·00913	0·890	0·01833
0·888	0·00909	0·907	0·01829
0·915	0·00911	0·923	0·01840
0·936	0·00913	0·937	0·01845

in rate, which is more marked in the slowest cases, is probably due to some specific action of the colloidal peroxide on the rate of escape of the gas (13).



The values at half decomposition are taken for comparison in this and the other series. It is seen from Table II that the rate is directly proportional to

the amount of catalyst used. The agreement is satisfactory, but owing to dilution of the catalyst for the lowest readings, and its addition in two lots for the highest readings, this series is much the least accurate of all.

Table II.

Amount of catalyst. a.	Velocity coefficient. k.	k/a.
2·5	0·00895	0·00358
5·0	0·0176	0·00352
7·5	0·0261	0·00348
10·0	0·0348	0·00348
12·5	0·0440	0·00352
15·0	0·0523	0·00349
	Mean	0·00351

A series of experiments was made in which the same sample of catalyst was used for a number of consecutive decompositions. After the experiment, the peroxide was allowed to settle and the supernatant liquid syphoned off. The peroxide was then washed twice by decantation in this way, after which it took too long to settle. It was then made up to 10 c.c. and used for another determination. The following are the values of k at half decomposition for one specimen :—

First time of usage	0·0265
Second time of usage	0·0256
Third time of usage	0·0248
Fourth time of usage	0·0241
Fifth time of usage	0·0235

There is, therefore, a slight decay in the catalytic activity. This is accounted for, in part, by the absorption of alkali, which was not removed during the washing of the peroxide after each experiment, but there is probably also a change in the nature of the surface owing to the continued chemical action taking place on it.

The Accelerating Effect of Sodium Chloride.

It was found that the rate of the reaction was accelerated by the addition of sodium salts, and the effect of sodium chloride has been examined quantitatively.

The solution for decomposition was made up to contain the requisite quantity of salt, pure sodium chloride, twice precipitated from brine by

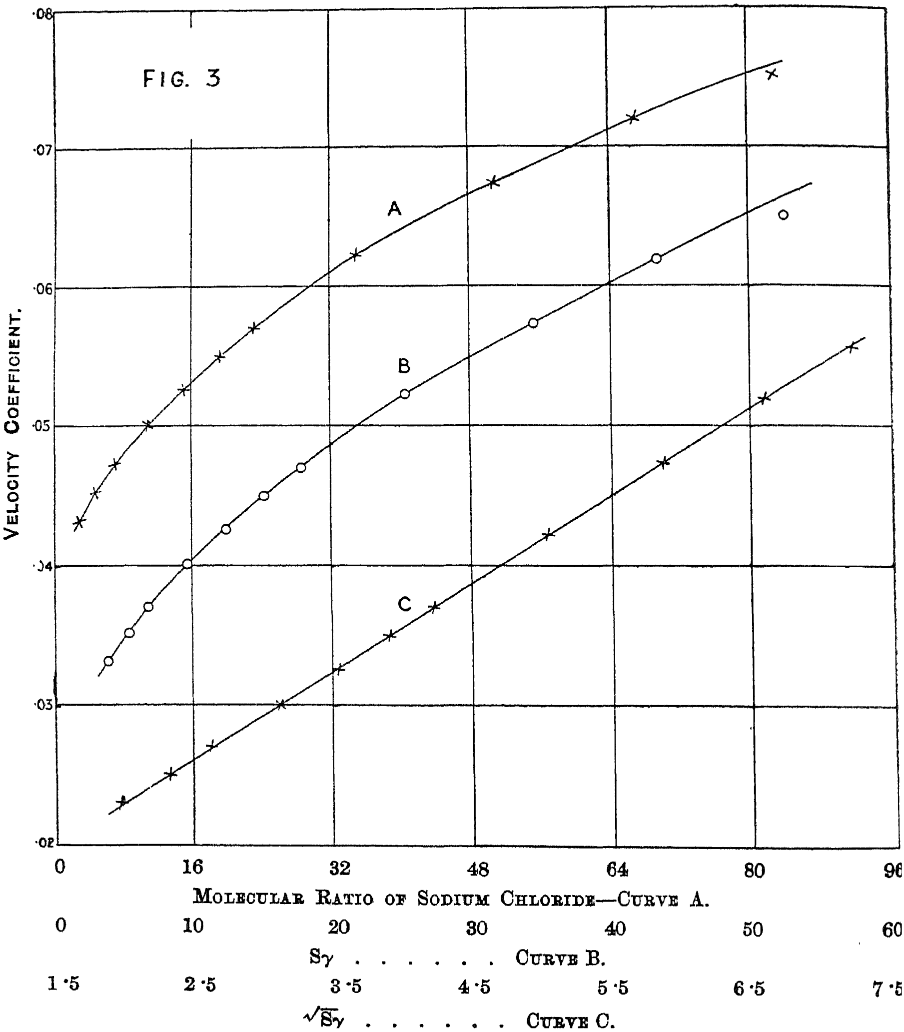
hydrochloric acid gas, being used. The quantities are expressed in terms of molecules taking the amount of sodium hypochlorite at half decomposition as unity. The results were plotted, and the values (to three significant figures), taken from the curves at equal intervals, are given in Table III. The velocity coefficient (at half decomposition), plotted against the amount of salt present, is shown in fig. 3, A.

Table III.

Fraction of the NaOCl decomposed.	Molecular ratio of NaCl present.										
	3.	5.	7.	11.	15.	19.	23.	35.	51.	67.	83.
0·10	0·0226	0·0245	0·0261	0·0291	0·0319	0·0340	0·0360	0·0410	0·0464	0·0508	—
0·20	0·0226	0·0246	0·0263	0·0294	0·0320	0·0343	0·0362	0·0413	0·0467	0·0510	0·0546
0·30	0·0227	0·0248	0·0265	0·0296	0·0321	0·0345	0·0364	0·0416	0·0469	0·0513	0·0550
0·40	0·0229	0·0250	0·0268	0·0298	0·0323	0·0348	0·0367	0·0419	0·0471	0·0516	0·0552
0·50	0·0231	0·0251	0·0270	0·0301	0·0326	0·0350	0·0370	0·0423	0·0474	0·0519	0·0556
0·60	0·0232	0·0253	0·0272	0·0303	0·0330	0·0353	0·0373	0·0427	0·0478	0·0523	0·0560
0·70	0·0233	0·0255	0·0275	0·0307	0·0335	0·0357	0·0378	0·0431	0·0484	0·0529	0·0566
0·80	0·0235	0·0258	0·0278	0·0311	0·0340	0·0362	0·0384	0·0438	0·0492	0·0536	0·0575
0·90	0·0237	0·0260	0·0282	0·0315	0·0346	0·0368	0·0390	0·0444	0·0500	0·0545	0·0586

No relationship can be traced between them directly, the effect being evidently ionic.

Arrhenius (14) first pointed out that the usual expression for the degree of dissociation of an electrolyte $\gamma = \lambda_v/\lambda_\infty$, should be corrected for the viscosity of the medium. The value $\gamma = \lambda_v/\lambda_\infty, \ \eta_v/\eta_0$, is often employed, but Washburn (15) has suggested $\gamma = \lambda_v/\lambda_\infty\,(\eta_v/\eta_0)^m$, where m is less than unity Green (16), in studying the conductivity of lithium chloride in the presence of varying amounts of sucrose, found $\gamma = \lambda_v/\lambda_\infty\,(\eta_v/\eta_0)^{\cdot 7}$ to give a very close approximation to the true ionisation over a wide range of viscosity, and this expression has been used in calculating the degree of ionisation of sodium chloride and sodium hydroxide in Tables IV and V respectively. In Table IV, all the values up to 1N are those given by Noyes and Falk (17); for the other concentrations the conductivity values are by Kohlrausch and Maltby (18), and the viscosity values by Lyle and Hosking (19). In Table V, all the values are by Bousfield and Lowry (20). These values were plotted, and the degrees of ionisation of all the solutions under consideration were read from the curves.



Vertical scale as printed is for Curve C. For Curves B and A begin one and two divisions higher respectively.

Table IV.

N.	λ.	η_v/η_0.	γ.
0·0	108·9	1·0000	—
0·1	91·96	1·0086	0·849
0·2	87·67	1·0167	0·814
0·5	80·89	1·041	0·764
1·0	74·31	1·086	0·723
2·0	64·8	1·167	0·663
3·0	56·5	1·320	0·630

Table V.

N.	λ.	η_v/η_0.	γ.
0·0	218	1·000	—
0·2522	184·5	1·041	0·870
0·5099	173·7	1·085	0·843
1·0420	156·3	1·185	0·807
1·3163	148·4	1·242	0·792
1·5961	140·5	1·306	0·7765
2·1722	125·6	1·453	0·7485
2·770	111·7	1·640	0·724
4·363	80·0	2·410	0·679

Table VI.

Molecular Ratio of NaOCl : Unity. Molecular Ratio of NaOH : 0·76.

Molecular ratio of.		Total concentration. Grm. mols./litre.	γ_{NaCl}.	γ_{NaOH}.	γ.	Sγ.	$\sqrt{S\gamma}$.	Velocity coefficient *k*.		Difference.
NaCl.	Total sodium compounds. S.							Observed.	Calculated.	
3·0	4·76	0·199	0·814	0·8775	0·824	3·922	1·980	0·0231	0·0230	+0·0001
5·0	6·76	0·283	0·7955	0·8655	0·8035	5·431	2·330	0·0251	0·0252	−0·0001
7·0	8·76	0·366	0·782	0·8565	0·7885	6·908	2·628	0·0270	0·0270	0·0000
11·0	12·76	0·534	0·7605	0·8415	0·7655	9·770	3·125	0·0301	0·0301	0·0000
15·0	16·76	0·701	0·7445	0·829	0·7485	12·55	3·542	0·0326	0·0328	−0·0002
19·0	20·76	0·868	0·7315	0·818	0·7345	15·25	3·905	0·0350	0·0350	0·0000
23·0	24·76	1·035	0·7205	0·8075	0·723	17·90	4·231	0·0370	0·0371	−0·0001
35·0	36·76	1·537	0·689	0·779	0·691	25·40	5·040	0·0423	0·0421	+0·0002
51·0	52·76	2·206	0·655	0·747	0·6565	34·63	5·884	0·0474	0·0474	0·0000
67·0	68·76	2·874	0·6325	0·720	0·6335	43·56	6·600	0·0519	0·0519	0·0000
83·0	84·76	3·543	0·620	0·695	0·621	52·64	7·255	0·0556	0·0560	−0·0004

The method of calculating the degree of ionisation of the mixed solution under investigation was as follows:—The total concentration of sodium compounds present was calculated. The degree of ionisation, γ_{NaCl}, of a solution of sodium chloride of this strength was taken from the curve, and similarly, γ_{NaOH}, for a solution of sodium hydroxide. The difference between the values was divided by the ratio of the sodium hydroxide to the total sodium compounds; this was added to the value γ_{NaCl}, and the result taken as representing very closely the true degree of dissociation, γ, of the mixture. The single molecule of sodium hypochlorite was reckoned as sodium chloride; the degree of ionisation of the two salts is very similar, and any difference soon becomes negligible in the presence of so great an excess of sodium

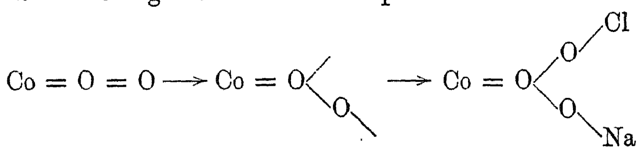
chloride. Since the amount of soda present is small, any error in the estimation of the dissociation is obviously small and eventually negligible.

The product of the total sodium compounds S, and the degree of dissociation γ, gives the sodium ions present in the solution. The rate plotted against $S\gamma$ is shown in fig. 3, B. The rate plotted against the square root of $S\gamma$ is a straight line (fig. 3, C). The equation to the line is

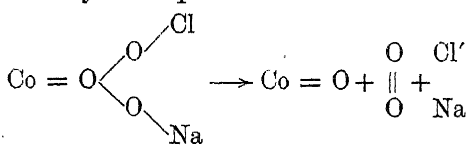
$$k = 0{\cdot}00625\sqrt{S\gamma} + 0{\cdot}0106,$$

and the agreement between the observed values and those calculated from the equation is seen from the last column in Table VI to be very close.

If this relationship be regarded as representing the adsorption of sodium ions by the peroxide, then the rate of the reaction is proportional to the amount adsorbed. The reaction is probably the result of the hypochlorite ion and sodium ion attaching themselves to the peroxide:—



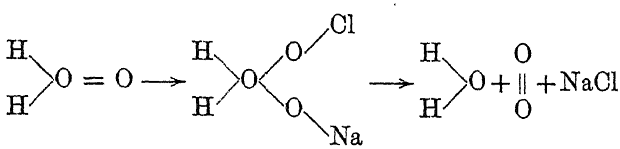
The resulting compound containing a quadrivalent oxygen atom is extremely unstable and immediately decomposes:—



The greater the concentration of sodium ions in the presence of a fixed amount of hypochlorite the quicker the reaction proceeds, and the rate will be proportional to the degree of "adsorption" of sodium ions on the oxygen atom.

The cobaltous oxide is immediately re-oxidised to the peroxide. It has been shown (11) that this reaction readily takes place, and is very rapid compared with the decomposition of the hypochlorite.

Herein the action differs from the corresponding reaction with hydrogen peroxide:



where the water is not re-oxidised by the hypochlorite. This explains why, with a metallic peroxide, the whole of the oxygen appears to come from the hypochlorite

$$2NaOCl \longrightarrow 2NaCl + O_2,$$

whereas with hydrogen peroxide one atom appears to come from each of the reactants :—

$$\mathrm{NaOCl} + \mathrm{H_2O_2} \longrightarrow \mathrm{NaCl} + \mathrm{H_2O} + \mathrm{O_2}.$$

Such a mechanism for this reaction receives support from Lowry's method of determining the nature of valency on the electronic basis (21). Cobalt peroxide would be represented as $\mathrm{Co}::\underset{\cdot\cdot}{\mathrm{O}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:$ The oxygen next the cobalt is one electron short of its complement and is therefore positively charged; the second has one electron in excess and is therefore negatively charged. Hence the two oxygen atoms are joined by one covalence and one electrovalence $\mathrm{Co} = \overset{+}{\mathrm{O}}-\overset{-}{\mathrm{O}}$ or $\mathrm{Co} = \mathrm{O}\begin{matrix}\diagup^{+}\\ \diagdown_{\mathrm{O}\diagdown_{-}}\end{matrix}$. One may therefore picture the negative hypochlorite ion attaching itself to the positive oxygen and the positive sodium ion to the negative oxygen.

The Retarding Effect of Alkali.

It is a well known fact that alkalis retard the decomposition of hypochlorites, and the same is true of their catalytic decomposition by cobalt peroxide.

In this series of experiments, all other conditions being constant, the decomposition was carried out in the presence of varying amounts of sodium hydroxide. The results are given in Table VII, and the values of k at half decomposition are plotted against the alkali present in fig. 4, A.

No direct relation can be found between the rate, or the decrease of rate, and the amount of soda present, without first allowing for the accelerating effect of the sodium ions added. The details of this are given in Table VIII. The degree of dissociation, γ, of the mixture is calculated as before. It may be noticed that the method gives an almost constant value; it is well known that the ionisation of a strong base is scarcely affected by the addition of a salt. The value of the sodium ions, $S\gamma$, is thus found, and the increase of rate expected from the addition is calculated from the relation already found (p. 144).

Table VII.

Fraction of the NaOCl decomposed.	Molecular ratio of NaOH present.										
	Nil.	0·404.	0·768.	1·072.	1·448.	2·220.	3·400.	3·980.	6·700.	11·20.	15·66.
0·10	0·0344	0·0267	0·0233	0·0215	0·0196	0·0171	0·0148	0·0139	0·0114	0·0094	0·0083
0·20	0·0345	0·0267	0·0234	0·0215	0·0196	0·0172	0·0148	0·0139	0·0114	0·0094	0·0082
0·30	0·0346	0·0268	0·0234	0·0215	0·0197	0·0172	0·0148	0·0140	0 0114	0·0094	0·0082
0·40	0·0347	0·0269	0·0235	0·0216	0·0197	0·0173	0·0149	0·0140	0·0114	0·0094	0·0082
0·50	0·0349	0·0270	0·0235	0·0216	0·0198	0·0173	0·0149	0·0140	0·0114	0·0094	0·0082
0·60	0·0350	0·0271	0·0237	0·0217	0·0198	0·0174	0 0149	0·0140	0·0114	0·0094	0·0082
0·70	0·0351	0·0273	0·0239	0·0219	0·0199	0·0175	0·0150	0·0143	0·0114	0·0095	0·0082
0·80	0·0353	0·0278	0·0242	0·0221	0·0199	0·0176	0·0152	0·0145	0·0115	0·0096	0·0082
0·90	0·0355	0·0281	0·0246	0·0224	0·0200	0·0178	0·0154	0·0147	0·0115	0·0097	0·0082

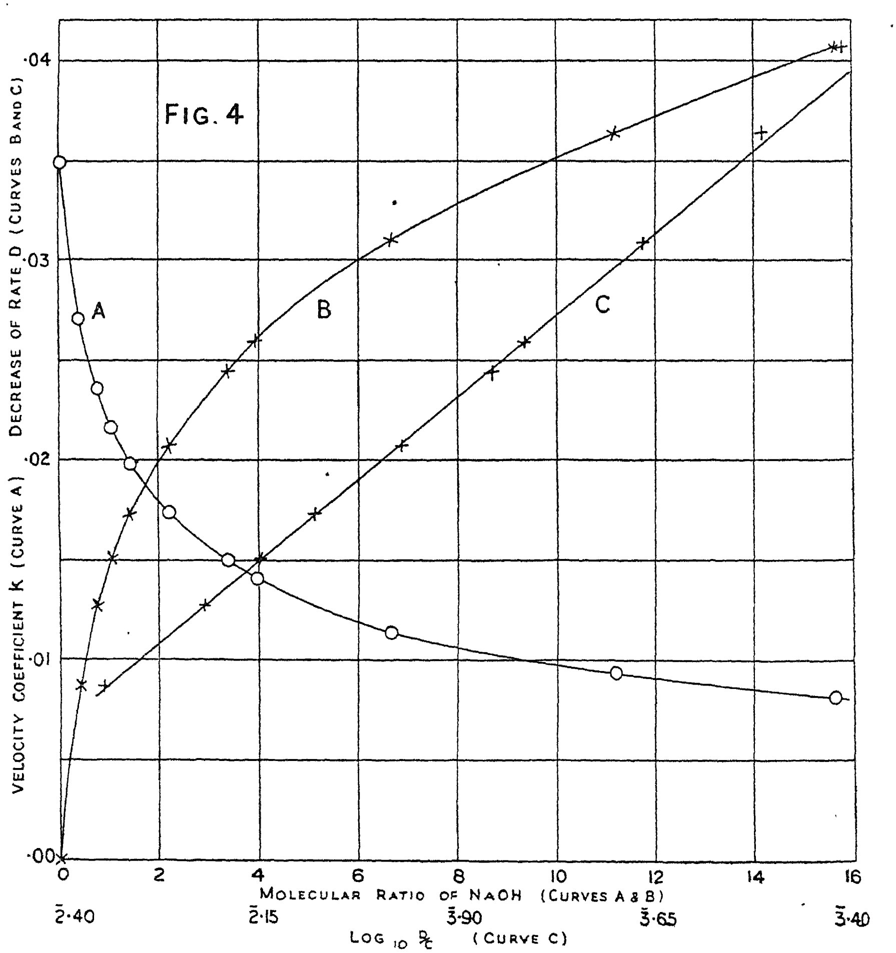


Table VIII.

Molecular Ratio of NaOCl : Unity. Molecular Ratio of NaCl : 3·0.

Molecular ratio of		Total concentration. Grm. mol./litre.	γ_{NaCl}.	γ_{NaOH}.	γ.	Sγ.	$\sqrt{S\gamma}$.	Increase of rate.
NaOH. C.	Total sodium compounds. S.							
Nil	4·000	0·179	0·818	0·881	0·818	3·273	1·768	—
0·404	4·404	0·197	0·814	0·878	0·820	3·612	1·900	0·0008
0·768	4·768	0·213	0·810	0·8755	0·8205	3·912	1·977	0·0013
1·072	5·072	0·227	0·807	0·8735	0·821	4·164	2·040	0·0017
1·448	5·448	0·224	0·8025	0·871	0·821	4·472	2·114	0·0022
2·220	6·220	0·278	0·795	0·865	0·820	5·100	2·258	0·0031
3·400	7·400	0·331	0·787	0·860	0·8205	6·071	2·464	0·0043
3·980	7·980	0·357	0·7825	0·857	0·820	6·543	2·558	0·0049
6·700	10·70	0·478	0·766	0·8455	0·816	8·732	2·955	0·0074
11·20	15·20	0·679	0·7465	0·830	0·808	12·28	3·504	0·0108
15·66	19·66	0·879	0·731	0·817	0·8075	15·88	3·985	0·0139

By adding these increases to the rate in absence of alkali, the increased rate due to the addition of the sodium ions (as sodium hydroxide) is found, and by subtracting the corresponding values of the observed rate, the decrease due to the hydroxyl ions is secured (Table IX). The decrease of rate plotted against the amount of alkali is shown in fig. 4, B.

Table IX.

Velocity coefficient k.		Decrease. D.	$\log_{10}$ D/C.	$\log_{10}$ D/C calculated.	Difference.
Increased.	Observed.				
0·0349	0·0349				
0·0357	0·0270	0·0087	$\bar{2}$·3331	$\bar{2}$·3333	−0·0002
0·0362	0·0235	0·0127	$\bar{2}$·2185	$\bar{2}$·2140	+0·0045
0·0366	0·0216	0·0150	$\bar{2}$·1459	$\bar{2}$·1432	+0·0027
0·0371	0·0198	0·0173	$\bar{2}$·0772	$\bar{2}$·0746	+0·0026
0·0380	0·0173	0·0207	$\bar{3}$·9696	$\bar{3}$·9714	−0·0018
0·0392	0·0149	0·0243	$\bar{3}$·8541	$\bar{3}$·8597	−0·0056
0·0398	0·0140	0·0258	$\bar{3}$·8117	$\bar{3}$·8145	0·0028
0·0423	0·0114	0·0309	$\bar{3}$·6639	$\bar{3}$·6602	+0·0037
0·0457	0·0094	0·0363	$\bar{3}$·5107	$\bar{3}$·4960	+0·0147
0·0488	0·0082	0·0406	$\bar{3}$·4137	$\bar{3}$·3660	+0·0477

If the decrease of rate is due to the adsorption of alkali and proportional to the amount adsorbed, then, by substituting the decrease of rate for the amount adsorbed in an adsorption isotherm, a relation should be found. The

isotherm suggested by Williams (22) was found to hold, for on plotting $\log D/C$ against D,

where $$D = \text{decrease of rate},$$

$$C = \text{molecular ratio of alkali},$$

a straight line is obtained (fig. 4, C). The linear relationship is given by the equation

$$\log_{10} D/C = -30{\cdot}\dot{3}\,D - 1{\cdot}4020,$$

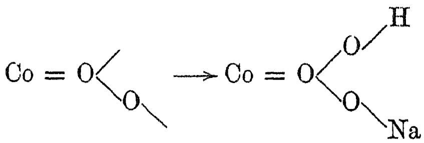
and the agreement between the observed and calculated values given in the last column of Table IX is seen to be very close, except in the case of the last two values.

Taking the extreme values in this series, and substituting them in the Freundlich isotherm,

$$D_2/D_1 = (C_2/C_1)^{1/n},$$

it is found that $n = 2{\cdot}22$, so that the adsorption of the hydroxyl ion is of the same order as that of the sodium ion (where $n = 2{\cdot}0$).

It is therefore evident that the effect of the alkali in retarding the decomposition is proportional to its adsorption on the peroxide, and appears to be due to the hydroxyl ions linking on to the positive oxygen valence, to the exclusion of the hypochlorite

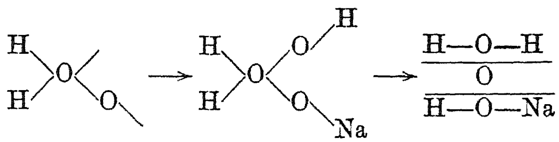


Such a molecule of peroxide is inactive, and incapable of effecting decomposition of the hypochlorite, because all its valencies are satisfied, and it is therefore unable to link on a hypochlorite ion.

It may be noted that the successful application, to the case of the addition of sodium hydroxide, of the relation found between the rate and the sodium ions present in the case of the addition of sodium chloride, lends further support to the suggested mechanism. It would appear also that the accelerating effect is due to the sodium ions without any (appreciable) retarding effect of the chlorine ions. Either the "life" of the chlorine ion on the positive valence is very short, or else this valence is capable of holding anions only through an oxygen atom, as, *e.g.*, OCl and OH. It is proposed to investigate the accelerating effect of other sodium salts, and so ascertain the relative retarding effects of the different anions.

The suggested mechanism would explain why hydrogen peroxide is comparatively stable in presence of acid, but readily decomposes in alkali solution.

In the latter case the hydroxyl ion is adsorbed by the positive valence, and the resulting quadrivalent oxygen compound at once decomposes—



In acid solution, the concentration of the hydroxyl ion is so depressed that such combination is comparatively negligible.

Temperature Coefficient.

The rate of the reaction was examined every five degrees from 25° to 50°, all other conditions being constant. The composition of the solution was the same as in the first series of experiments (p. 138), and 10 c.c. of catalyst were employed.

Table X.

Fraction of the NaOCl decomposed.	Velocity coefficient k at					
	25°.	30°.	35°.	40°.	45°.	50°.
0·10	0·0090	0·0144	0·0219	0·0338	0·0520	0·0795
0·20	0·0091	0·0142	0·0217	0·0339	0·0522	0·0798
0·30	0·0092	0·0142	0·0218	0·0340	0·0525	0·0801
0·40	0·0092	0·0143	0·0220	0·0341	0·0527	0·0804
0·50	0·0093	0·0144	0·0222	0·0342	0·0530	0·0806
0·60	0·0094	0·0146	0·0224	0·0344	0·0533	0·0810
0·70	0·0095	0·0149	0·0226	0·0346	0·0535	0·0818
0·80	0·0097	0·0151	0·0228	0·0349	0·0538	0·0831
0·90	0·0099	0·0153	0·0232	0·0357	0·0548	0·0862

The results are given in Table X, and the values at half decomposition are plotted against the temperature in fig. 5, A. The temperature coefficient for 10° is

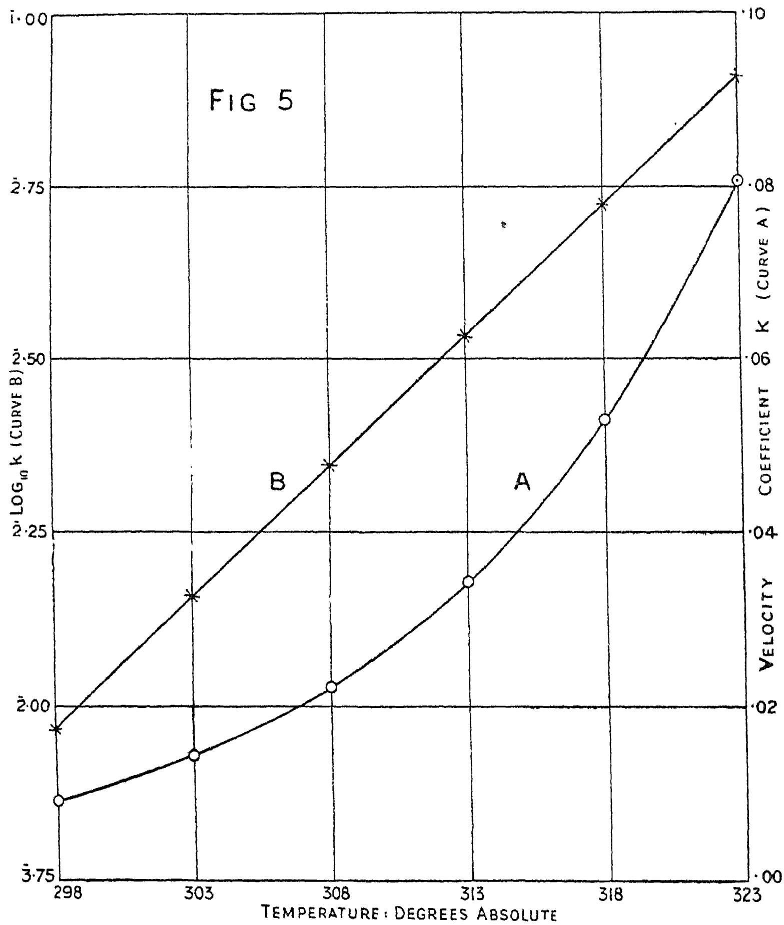
25°–35°	2·374
30°–40°	2·376
35°–45°	2·387
40°–50°	2·358
Mean	2·374

This high value shows that the reaction is not a diffusive one, for reactions in which the rate is determined by the rate of diffusion of the reactants through a layer are characterised by a low temperature coefficient. The high

temperature coefficient of this reaction supports the view that it consists in direct combination of the sodium and hypochlorite ions with the peroxide.

A linear relationship is obtained on plotting log k against the temperature (fig. 5, B). The equation to the line is

$$\log_{10} k = 0{\cdot}0376\,\mathrm{T} - 13{\cdot}2348,$$



and the agreement between the observed and calculated values is seen from Table XI. Introducing the observed values at 25° and 50° into the Arrhenius expression :—

$$\log_e \frac{k_{\mathrm{T}_2}}{k_{\mathrm{T}_1}} = \frac{\mathrm{E}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right)$$

the value is obtained for the energy of activation E = 16,574.

Table XI.

Absolute temperature T.	Velocity coefficient *k*.	$\text{Log}_{10}\ k$.	$\text{Log}_{10}\ k$ calculated.	Difference.
298	0·0093	$\bar{3}$·9685	$\bar{3}$·9700	−0·0015
303	0·0144	$\bar{2}$·1584	$\bar{2}$·1580	+0·0004
308	0·0222	$\bar{2}$·3464	$\bar{2}$·3460	+0·0004
313	0·0342	$\bar{2}$·5340	$\bar{2}$·5340	0·0000
318	0·0530	$\bar{2}$·7243	$\bar{2}$·7220	+0·0023
323	0·0806	$\bar{2}$·9063	$\bar{2}$·9100	−0·0037

Effect of Poisons.

The reaction was carried out in the presence of various substances which commonly poison a catalyst. The concentrations in each case were 10^{-4} gram-molecules per litre, but in no case could any appreciable effect be found, as is shown by the following figures for the velocity coefficient at half decomposition:—

No poison	0·0237
Hydrogen sulphide	0·0237
Potassium cyanide	0·0237
Mercuric chloride	0·0234
Arsenious oxide	0·0234

The peroxide is therefore particularly resistant to poisoning. This may be attributed to oxidation of the poison in the case of the sulphide and cyanide, but the immunity would appear to be due to the fact that the reaction consists in a true chemical combination between the catalyst and the reactants, and is not a purely surface action.

Summary.

1. The rate of decomposition of sodium hypochlorite solution by cobalt peroxide is directly proportional to the amount of peroxide present.

2. The rate is accelerated by sodium salts and (in the case of sodium chloride) is directly proportional to the square root of the concentration of sodium ions present. This is explained by assuming the mechanism of the reaction to consist in the linkage of hypochlorite ions to the positive oxygen and sodium ions to the negative oxygen of the peroxide, with subsequent immediate decomposition of the quadrivalent oxygen compound. In the presence of a fixed amount of hypochlorite, the rate is then proportional to the degree of adsorption of the sodium ions.

3. The rate is retarded by alkali and the retardation is proportional to the

adsorption of hydroxyl ions. This is explained by the fact that hydroxyl ions are attracted by the positive oxygen of the peroxide, yielding an inactive compound to the exclusion of hypochlorite ions.

4. The rate of the reaction has been measured beween 25° and 50°. The average temperature coefficient over this range is 2·37 and the Arrhenius activation coefficient E = 16,574.

5. The catalyst is not affected by any of the common catalytic poisons.

The author would express his thanks to Prof. Lowry for granting him every facility for carrying out this work and for his kind and sympathetic encouragement. He is indebted to the Royal Commissioners for the Exhibition of 1851 for a scholarship grant during this investigation.

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On the Scattering of X- and γ-Rays by Rings of Electrons.—The Effect of Damping of the Incident Radiation.

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(Received February 23, 1923.)

1. The object of the present investigation is to examine whether damping of the incident radiation can account for the abnormally small scattering of hard γ-rays by aluminium, iron and lead, which was observed by Ishino and was left unexplained in a previous investigation,* based on the hypothesis that scattering is a phenomenon of the diffraction by electron rings in the atom of undamped simple harmonic wave-trains of high frequency.

It may be stated at once that the result of the enquiry is negative : it is true that damping of an amount small enough to be consistent with the generation of moderately sharp lines in the X- and γ-ray spectrum *diminishes* the scattering of *long* waves, but it *increases* that of *short* waves, and in each case the change is far too small to explain Ishino's result. On the other hand, very large damping probably diminishes the scattering of all waves, but it is practically certain that it does not diminish it below the amount required by the Simple Pulse theory, whilst Ishino's values are only of the order of one-quarter of that amount. This result was to be expected, since an infinitely damped wave-train may be regarded as equivalent to a pulse.

If we wish to retain the electron ring theory of atomic structure, we are driven to the conclusion that some at least of the rings in aluminium, iron and lead are moving with speeds comparable with that of light. That this hypothesis affords some prospect of explaining Ishino's small scattering is evident from the fact that the scattering coefficient on all the theories considered in the previous investigation has m^2—the square of the effective mass of the electron—as a factor in the denominator. If we adopt the Lorentz formula for the *transverse* mass—an assumption of doubtful validity in this connection—we must multiply the scattering coefficient by $1 - \beta^2$, in the usual notation ; we can then account for Ishino's small values by assuming that β is of the order $\frac{1}{2}\sqrt{3}$, or 0·866, which is not impossible in view of the values of β found for electrons from radioactive substances. Recent measurements of the X spectra of the heavy elements support this conclusion.† With such high speeds the whole of the previous investigation is nugatory, and a much more complete enquiry

* Schott, 'Roy. Soc. Proc.,' A, vol. 96, p. 395 (1920).

† Siegbahn, 'Phil. Mag.,' vol. 37, p. 601.

becomes necessary; in view of its difficulty it must be reserved for another investigation.

Values of β comparable with that just indicated are extremely unlikely to occur in the case of light atoms, such as hydrogen, helium, lithium and boron, for reasons sufficiently well known not to be insisted upon here. Hence it is of great theoretical importance to examine by experiment whether such small values of the scattering as those found by Ishino occur with these elements also; it has been pointed out previously that experiments of this kind would, if successful, afford a means of deciding between the Electron ring and Ring electron theories of atomic structure.

2. *Specification of the incident radiation.*—We shall make the same assumptions and use the same notation as before, but shall assume in addition that the incident waves are damped according to the usual exponential law. Other laws of damping are of course conceivable, but may be expected to produce analogous effects. Thus we shall assume that the electric and magnetic forces in the incident radiation are given by equations of the type

$$\left.\begin{aligned} &d_{\mathrm{A}} = h_{\mathrm{B}} = 0,\ d_{\mathrm{B}} = -h_{\mathrm{A}} = 0,\ t < t_0 \\ &d_{\mathrm{A}} = h_{\mathrm{B}} = \Sigma a \exp\{-\kappa(t-t_0)\}\cos\{\nu(t-t_0)+\epsilon\},\ t > t_0 \\ &d_{\mathrm{B}} = -h_{\mathrm{A}} = \Sigma b \exp\{-\kappa(t-t_0)\}\sin\{\nu(t-t_0)+\epsilon\},\ t > t_0 \end{aligned}\right\} \tag{1}$$

where the damping coefficient κ, like the frequency ν, is the same for all the waves, whilst the amplitudes a, b, the epoch ϵ, and the time of incidence of the train, t_0, vary from train to train, the two latter quite irregularly.

The intensity of the incident radiation is best measured by the total amount of energy which falls on unit area perpendicular to the direction of incidence in all the wave-trains incident per unit time, *e.g.* for all values of t_0 between zero and unity. On account of the irregular distribution of t_0, ϵ and α (the polarisation azimuth previously defined) we may find the total energy of each wave-train separately and add the separate energies for unit time. Thus we obtain—

$$\begin{aligned} \mathrm{I} &= \Sigma\,(c/4\pi)\int_{t_0}^{\infty}(d_{\mathrm{A}}h_{\mathrm{B}} - d_{\mathrm{B}}h_{\mathrm{A}})\,dt \\ &= \Sigma\,(c/8\pi)\int_{t_0}^{\infty}[a^2+b^2+(a^2-b^2)\cos 2\{\nu(t-t_0)+\epsilon\}]\exp\{-2\kappa(t-t_0)\}\,dt \\ &= \Sigma\,c\,(a^2+b^2)/16\pi\kappa \end{aligned} \tag{2}$$

where the terms involving $\cos 2\epsilon$ and $\sin 2\epsilon$ disappear on averaging, and the summation is for all the wave-trains incident in unit time.

3. The distinguishing characteristic of the new specification (1) is the discontinuity of the electric and magnetic forces and of the resulting disturbance of the electron ring. Not only will forced vibrations be generated, of the same frequency and with the same damping coefficient as the incident radiation, but also free vibrations, with the frequencies and damping coefficients characteristic of the ring. The former correspond to the true scattered radiation of unaltered type, the latter to fluorescent or resonance radiation; in this way the change of type observed by Florance, a softening of the hard γ rays employed by him, may be accounted for qualitatively. To calculate the intensity of the fluorescent radiation we must have a detailed knowledge, not only of the structure of the electron ring, but also of the forces controlling its motion and determining its free periods. In the absence of this knowledge we must perforce confine ourselves to a study of the scattered radiation; this can be carried out provided that we assume as before that the frequency of the incident radiation is so great compared with those of the free vibrations that the controlling forces of the atom may be neglected in comparison with the effective forces of the electrons in the disturbed motion.

4. As in other cases of discontinuous motion, difficulties arise in the calculation of the resulting distant electro-magnetic field, but these may be avoided by the artifice of replacing the expressions (1) by the equivalent Fourier integrals. We find—

$$\left.\begin{aligned} d_A = h_B &= \Sigma\pi^{-1} a \int_0^\infty \int_{t_0}^\infty \exp\{-\kappa(\xi - t_0)\} \cos\{\nu(\xi - t_0) + \epsilon\} \\ &\qquad\qquad \cos\eta(\xi - t)\, d\xi\, d\eta \\ &= \Sigma \int_{-\infty}^{\infty} a' \cos(\eta t + \epsilon')\, d\eta \\ d_B = -h_A &= \Sigma \int_{-\infty}^{\infty} b' \sin(\eta t + \epsilon')\, d\eta \end{aligned}\right\} \quad (3)$$

where

$$(a', b') = (a, b)/2\pi\sqrt{\{\kappa^2 + (\eta - \nu)^2\}}, \quad \epsilon' = \epsilon - \eta t_0 - \tan^{-1}\{(\eta - \nu)/\kappa\}. \quad (4)$$

Thus the assumed damped incident radiation is analysed into an infinite series of undamped simple harmonic wave-trains of the same type as those assumed in §6 of the previous investigation, but *all* frequencies are now represented. Hence the assumption that the incident frequency is large compared with the free frequencies of the ring is no longer true, and we must examine what error is likely to arise in consequence.

5. The expressions (4), § 4, are of the familiar type which occurs in the theory

of resonance of a system with one degree of freedom. The amplitudes (a, b') have maxima for $\eta = \nu$, the frequency of the actual incident vibration, and these maxima increase in sharpness as κ diminishes. Retaining our original assumption, that all the free frequencies of the ring are small compared with ν, we see that (a', b') have comparatively small values for those values of η, which are liable to cause resonance in the ring, and for which the method of the previous investigation becomes inaccurate. Even when κ is as large as $\nu/2\pi$, which corresponds to a logarithmic decrement equal to one-half, and is quite inconsistent with the generation even of diffuse spectrum lines, the values of (a', b') for small values of η are only $\kappa/\nu\,(\kappa^2 + \nu^2)$, or less than $0{\cdot}16$ times their maximum values, and the corresponding energy is only one-fortieth of its maximum. Hence for a damping of this order or less, the method of the previous investigation may be applied to (3), § 4, without danger of serious error.

6. *Specification of the scattered radiation.*—By means of the process used in §§ 11–14 of the previous investigation, we obtain from (3), §4, the following expressions for the sums of the accelerations **f** of the electrons of the ring and of their components (**Uf**) in the direction of the unit vector—

$$\left.\begin{aligned}
\Sigma f &= \frac{en}{2m}\,\Sigma\sum_{-\infty}^{\infty}\int_{-\infty}^{\infty}\{\cos\psi\,(a'\cos\alpha + \iota b'\sin\alpha),\ a'\sin\alpha - \iota b'\cos\alpha,\\
&\qquad\qquad -\sin\psi\,(a'\cos\alpha + \iota b'\sin\alpha)\}\\
&\qquad .\,\mathrm{J}_{\kappa n}(2\tau\sin\tfrac{1}{2}\theta\sin\gamma)\exp\iota\Omega\,d\eta.\\
\Sigma(\mathrm{U}f) &= \frac{en}{2m}\,\Sigma\sum_{-\infty}^{\infty}\int_{-\infty}^{\infty}\{\cos(\kappa\mathrm{U})\,(a'\cos\alpha + \iota b'\sin\alpha) + \cos(y\mathrm{U})\\
&\qquad\qquad .\,(a'\sin\alpha - \iota b'\cos\alpha)\}\\
&\qquad .\,\mathrm{J}_{\kappa n}(2\tau\sin\tfrac{1}{2}\theta\sin\gamma)\exp\iota\Omega\,d\eta.\\
\text{where }\Omega &= (\eta + kn\omega)(t - \mathrm{R}/c) + \epsilon' + kn(\delta + v - \tfrac{1}{2}\pi),\quad \tau = \eta\rho/c\,;
\end{aligned}\right\}\quad(5)$$

whilst conjugate complex terms have to be added so as to make the whole real.

The notation is the same as before, with the exception that η replaces ν in the definition of τ, whilst a', b', and ϵ', defined by (4), § 4, replace a, b, and ϵ respectively.

The distant field is given by (7), § 9, of the previous investigation on the basis of the assumption just stated in § 5, so that the Poynting flux is given by (16), § 15, *i.e.* by

$$\mathbf{P} = \frac{e^2}{4\pi c^3 \mathrm{R}^2}[\{\Sigma\mathbf{f}\}^2 - \{\Sigma(\mathbf{Uf})\}^2]\,\mathbf{U}. \tag{6}$$

7. *Determination of the scattered radiation.*—In order to determine S, the average energy scattered in the direction **U** per unit time per unit solid angle,

we multiply (6), § 6, scalarly by $R^2\mathbf{U}$, and average the result with respect to the time t, the epoch ϵ, and the polarisation azimuth α just as before, but some modification in the process is necessary on account of the integration with respect to η in (5), § 6.

Each of the components of $\Sigma\mathbf{f}$, as well as the scalar quantity $\Sigma\ (\mathbf{Uf})$, is of the form

$$X = \Sigma \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} [A \exp \iota\Omega + A' \exp (-\iota\Omega)]\, d\eta,$$

where A, A′ are conjugate complex coefficients involving η, κ, ν, a', b', α, ψ, θ and γ, but not t or ϵ, whilst Ω is a function of η, k, t, ϵ' determined by (5), § 6. Integrating X^2 with respect to the time, we obtain

$$\int_{-T}^{T} X^2\, dt = \Sigma \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-T}^{T} [A_1 A_2' \exp \iota (\Omega_1 - \Omega_2) \\ + A'_1 A_2 \exp \{-\iota (\Omega_1 - \Omega_2)\}]\, d\eta_1\, d\eta_2\, dt,$$

where η_1, k_1 and η_2, k_2 are different pairs of values of η, k, and Ω_1, Ω_2 corresponding values of Ω. Terms involving exponentials of the type $\exp \iota (\Omega_1 + \Omega_2)$ have been omitted, because they involve $\exp (\pm 2\iota\epsilon')$ as a factor and disappear on averaging with respect to the epoch ϵ, as we see from (4), § 4. Bearing in mind (5), § 6, and performing the integration with respect to t, we obtain

$$\int_{-T}^{T} X^2\, dt = 2\Sigma \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\sin T\zeta}{\zeta} [A_1 A_2' \exp \iota \{\zeta R/c \\ + (k_1 - k_2)\, n\, (\delta + \upsilon - \tfrac{1}{2}\pi)\} \\ + A_1' A_2 \exp (-\iota \{\zeta R/c + (k_1 - k_2)\, n\, (\delta + \upsilon - \tfrac{1}{2}\pi)\})]\, d\eta\, d\zeta,$$

where we have written, for the sake of brevity,

$$\eta = \tfrac{1}{2} (\eta_1 + \eta_2), \qquad \zeta = \eta_2 - \eta_1 - (k_1 - k_2)\, n\omega.$$

When T becomes infinitely great, the ζ-integral becomes one of Dirichlet's type, and reduces to π times the value for $\zeta = 0$ of the factor of $\sin T\zeta/\zeta$ under the sign of integration. Since η_1, η_2 are generally incommensurable with ω, $\zeta = 0$ requires both $\eta_1 = \eta_2 = \eta$ and $k_1 = k_2 = k$, say. Thus A_1, A_2 both reduce to A, and A_1', A_2' to A′, and we obtain finally

$$\int_{-\infty}^{\infty} X^2\, dt = 4\pi\Sigma \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} AA'\, d\eta. \tag{7}$$

This result is analogous to one due to Rayleigh and Schuster.

8. The operation (7), § 7, is to be applied to each term of the scalar product R^2 (**PU**) derived from (6), § 6, bearing in mind (5), § 6. Thus we must put

$$A = \frac{en}{2m} \cos \psi \, (a' \cos \alpha + \iota b' \sin \alpha) \, J_{kn} (2\tau \sin \tfrac{1}{2}\theta \sin \gamma),$$

and the remaining three analogous quantities, which occur in (5), in succession, and we must bear in mind that (a', b') are functions of the amplitudes (a, b) and of the variable η in accordance with (4), § 4. Thus we find

$$\int_{-\infty}^{\infty} \{\Sigma \mathbf{f}\}^2 \, dt = \frac{\pi e^2 n^2}{m^2} \Sigma \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} (a'^2 + b'^2) \, J_{kn}{}^2 (2\tau \sin \tfrac{1}{2}\theta \sin \gamma) \, d\eta,$$

$$\int_{-\infty}^{\infty} \{\Sigma (\mathbf{U}\mathbf{f})\}^2 \, dt = \frac{\pi e^2 n^2}{m^2} \Sigma \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} [a'^2 \{\cos (\kappa \mathrm{U}) \cos \alpha + \cos (y\mathrm{U}) \sin \alpha\}^2$$
$$+ b'^2 \{\cos (\kappa \mathrm{U}) \sin \alpha - \cos (y\mathrm{U}) \cos \alpha\}^2] \, J_{kn}{}^2 \, d\eta.$$

These expressions must now be averaged for the epoch ϵ, a process which leaves both unaltered, since ϵ has disappeared in the time averaging, and for the polarisation azimuth α, leaving the first unaltered, but replacing $\cos^2 \alpha$ and $\sin^2 \alpha$ in the second by one-half and $\cos \alpha \sin \alpha$ by zero. Proceeding exactly as in the previous investigation, § 15, but using (4), § 4, we obtain

$$S = \frac{e^4 n^2}{32\pi^2 c^3 m^2} \Sigma \sum_{-\infty}^{\infty} (a^2 + b^2)(1 + \cos^2 \theta) \int_{-\infty}^{\infty} \frac{J_{kn}{}^2 (2\tau \sin \frac{1}{2}\theta \sin \gamma) \, d\eta}{\kappa^2 + (\eta - \nu)^2} \quad (7\mathrm{A})$$

which takes the place of (18), § 15, in the previous investigation and gives the scattering at an angle θ to the direction of the incident radiation.

9. *The total scattering coefficient.*—We shall confine the remainder of our investigation to the determination of the total scattering coefficient of the ring, because Ishino's measurements were made on the total scattering, and other phenomena, such as asymmetry, are of no interest in this connection.

Since the intensity of the incident radiation is given by (2), § 2, we find that the scattering coefficient of the ring for the direction θ is given by

$$s = \frac{S}{I} = \frac{\kappa e^4 n^2 (1 + \cos^2 \theta)}{2\pi c^4 m^2} \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{J_{kn}{}^2 (2\tau \sin \frac{1}{2} \theta \sin \gamma) \, d\eta}{\kappa^2 + (\eta - \nu)^2}$$
$$= \frac{e^4 n (1 + \cos^2 \theta)}{2c^4 m^2} \left[1 + \sum_{1}^{n-1} \frac{\kappa}{\pi} \int_{-\infty}^{\infty} \frac{J_0 \{4\tau \sin (\pi i/n) \sin \frac{1}{2} \theta \sin \gamma\} \, d\eta}{\kappa^2 + (\eta - \nu)^2} \right] \quad (8)$$

This equation is obtained by the process of § 16 of the previous investigation and takes the place of (19). We see at once that for a single electron, $n = 1$, the integral terms involving the damping coefficient κ disappear. Hence we

conclude that *damping of the incident radiation has no effect whatever on the scattering of high frequency rays by hydrogen.*

10. Bearing in mind the definition of the Bessel Function J_0 we can transform (8), § 9, so as to effect the integration. For convenience sake we write, with l for logarithmic decrement,

$$\left.\begin{aligned} x &= 2(\nu\rho/c)\sin(\pi i/n), \quad y = 2(\kappa\rho/c)\sin(\pi i/n) = lx/\pi, \quad z = x + \iota y \\ \eta &= \nu + \kappa\xi, \quad 2\tau\sin(\pi i/n) = 2(\eta\rho/c)\sin(\pi i/n) = x + y\xi \end{aligned}\right\} \tag{9}$$

Then we find in succession—

$$\frac{\kappa}{\pi}\int_{-\infty}^{\infty}\frac{J_0\{4\tau\sin(\pi i/n)\sin\tfrac{1}{2}\theta\sin\gamma\}d\eta}{\kappa^2+(\eta-\nu)^2} = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{J_0\{2(x+y\xi)\sin\tfrac{1}{2}\theta\sin\gamma\}\,d\xi}{1+\xi^2}$$

$$= \frac{4}{\pi^2}\int_0^{\pi/2}\int_0^{\infty}\frac{\cos(2x\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi)\cos(2y\xi\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi)\,d\phi\,d\xi}{1+\xi^2}. \tag{10}$$

The ξ integral is well known, and its value is—

$$\tfrac{1}{2}\pi\exp(-2y\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi).$$

Hence the expression (10) becomes in succession—

$$\frac{2}{\pi}\int_0^{\pi/2}\cos(2x\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi)\exp(-2y\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi)\,d\phi$$

$$= \text{Real Part of } \frac{2}{\pi}\int_0^{\pi/2}\exp(2\iota z\sin\tfrac{1}{2}\theta\sin\gamma\sin\phi)$$

$$= \text{Real Part of } \{J_0(2z\sin\tfrac{1}{2}\theta\sin\gamma) + \iota K(2z\sin\tfrac{1}{2}\theta\sin\gamma)\} \tag{11}$$

where K denotes the function introduced by Rayleigh.*

Using (10) and (11) in (8), § 9, we obtain

$$s = \frac{e^4 n(1+\cos^2\theta)}{2c^4 m^2}\Big[1 + \text{Real Part of }\sum_1^{n-1}\{J_0(2z\sin\tfrac{1}{2}\theta\sin\gamma) + \iota K(2z\sin\tfrac{1}{2}\theta\sin\gamma)\}\Big] \tag{12}$$

The frequency ν and damping coefficient κ only occur implicitly in the complex variable z defined by (9).

When there is no damping, κ and y vanish, z reduces to its real part x, both the functions J_0 and K become real, and (12) reduces to (19), § 16, of the previous investigation.

When there is infinite damping, κ and y are infinitely great, the first integral in (11) obviously vanishes, every term of the sum in (12) disappears, and we obtain the scattering coefficient appropriate to the Simple Pulse Theory.

* 'Sound,' vol. 2, p. 164, eq. (5).

11. In order to obtain the mean scattering coefficient in the direction θ for an irregularly orientated assemblage of electron rings we multiply (12), § 10, by $\frac{1}{2}\sin\gamma\, d\gamma$ and integrate from 0 to π, just as in § 19 of the previous investigation. Using the well-known expansion in ascending powers of the argument of J_0 and Rayleigh's corresponding expansion of K, and writing u in place of $\sin\frac{1}{2}\theta$ as before, we obtain in succession—

$$\bar{s} = \frac{e^4 n\,(1+\cos^2\theta)}{2c^4 m^2}\left[1 + \text{Real Part of} \sum_1^{n-1} \frac{\exp(2\iota z \sin\frac{1}{2}\theta) - 1}{2\iota z \sin\frac{1}{2}\theta}\right]$$

$$= \frac{e^4 n\,(1 - 2u^2 + 2u^4)}{c^4 m^2}\left[1 + \text{Real Part of} \sum_1^{n-1} \frac{\exp(2\iota z u) - 1}{2\iota z u}\right]. \quad (13)$$

To find the total scattering coefficient S we must multiply (13) by $2\pi\sin\theta\, d\theta$, or $8\pi u\, du$, and integrate from $\theta = 0$ to $\theta = \pi$, or from $u = 0$ to $u = 1$. In this way we obtain

$$S = \frac{8\pi e^4 n}{3c^4 m^2}\left[1 + \text{Real Part of} \sum_1^{n-1} \frac{3}{4z^2}\left\{\frac{22}{15}\iota z + 1 + \frac{1}{z^2} + \frac{3}{z^4} - \left[1 - \frac{5}{z^2} + \frac{3}{z^4} - \frac{2}{\iota z}\left(1 - \frac{3}{z^2}\right)\right]\exp 2\iota z\right\}\right]. \quad (14)$$

This expression reduces to (26), § 20, of the previous investigation when there is no damping. Like that expression it may be expressed in terms of Bessel Functions of half integral order. With the notation of B.A. Report, 1914, p. 87, we write—

$$\left.\begin{aligned} &S_0(z) = \sin z, \quad S_1(z) = \frac{\sin z}{z} - \cos z, \quad S_2(z) = \left(\frac{3}{z^2} - 1\right)\sin z - \frac{3\cos z}{z} \\ &E_0'(z) = \epsilon^{\iota z}, \quad E'_1(z) = \left(\frac{1}{z} - \iota\right)\epsilon^{\iota z}, \quad E'_2(z) = \left(\frac{3}{z^2} - \frac{3\iota}{z} - 1\right)\epsilon^{\iota z} \end{aligned}\right\} \quad (15)$$

$E'(z)$ denotes the conjugate of $E(z)$ and is equal to $C(z) + \iota S(z)$.

Then we find from (14)—

$$S = \frac{8\pi e^4 n}{3c^4 m^2}\left[1 + \text{Real Part of} \sum_1^{n-1} \{E'_0(z)\, S_0(z) + \tfrac{1}{2}E'_2(z)\, S_2(z) - \tfrac{11}{10}z\}/\iota z^2\right]. \quad (16)$$

Unfortunately the E′ and S functions have not been tabulated for complex values of z, so that (16) is not available for numerical computation like the corresponding expression (28), § 20, of the previous investigation.

12. In order to obtain an expression suitable for numerical computation we shall write

$$x = r\cos\theta, \quad y = r\sin\theta, \quad r = \{2\sqrt{(\nu^2 + \kappa^2)}\,\rho/c\}\sin(\pi i/n), \quad \tan\theta = l/\pi \quad (17)$$

where l denotes the logarithmic decrement, as in (9), § 10. Thus r, θ may be

regarded as polar co-ordinates in the plane of the complex variable z, which is the argument in (14) and (16), § 11.

Further let us write for the sake of brevity—

$$\left.\begin{aligned} A &= \tfrac{2}{1}\tfrac{2}{5} r \sin\theta + \cos 2\theta + r^{-2}\cos 4\theta + 3r^{-4}\cos 6\theta \\ B &= \cos 2\theta - 5r^{-2}\cos 4\theta + 3r^{-4}\cos 6\theta + 2r^{-1}\sin 3\theta - 6r^{-3}\sin 5\theta \\ C &= \sin 2\theta - 5r^{-2}\sin 4\theta + 3r^{-4}\sin 6\theta - 2r^{-1}\cos 3\theta + 6r^{-3}\cos 5\theta \\ F(r,\theta) &= \tfrac{3}{4}r^{-2}\{A - [B\cos(2r\cos\theta) + C\sin(2r\cos\theta)]\exp(-2r\sin\theta)\} \end{aligned}\right\} \quad (18)$$

Then (14), § 11, may be written in the form—

$$S = S_1 n\left\{1 + \sum_{1}^{n-1} F(r,\theta)\right\}, \qquad S_1 = 8\pi e^4/3c^4m^2, \qquad (19)$$

S_1 denotes the scattering coefficient of a ring of one electron, *i.e.* the atomic scattering coefficient of hydrogen.

The expression (19) is convenient for numerical computation when r is greater than unity, but for smaller values it does not give sufficiently accurate results without very great labour.

In order to obtain a series of ascending powers of r we have recourse to (13), § 11, expand the right-hand member in an absolutely convergent series of ascending powers of zu, integrate term by term and in the resulting expression replace z by its value $r \exp \iota\theta$ in accordance with (17). When we compare the resulting equation with (19), we find

$$F(r,\theta) = \sum_{0}^{\infty}(-1)^j \frac{3(j^2+3j+4)}{(j+2)(j+3)(2j+2)!}(2r)^{2j}\cos 2j\theta$$

$$- \sum_{0}^{\infty}(-1)^j \frac{3(4j^2+16j+23)}{(2j+5)(2j+7)(2j+3)!}(2r)^{2j+1}\sin(2j+1)\theta. \quad (20)$$

13. *Numerical values.*—The function F defined by the equations (18)–(20) of § 12 may be called the scattering function, because it determines the proportional amount by which the scattering coefficient of a ring of electrons exceeds the value given by the Simple Pulse Theory, namely nS_1. For helium $n = 2$, and the function F itself gives the fractional excess scattering in question; for larger values of n we must take the sum of $n - 1$ functions F for the values $i = 1, 2, \ldots n-1$ in (17), § 12.

Since F is a function of two variables (x, y) or (r, θ) as the case may be, it can be represented by the ordinates of a surface erected above the (x, y) plane, or more simply by a contour-lined chart of this surface, the contour lines being of course the curves of constant F. Since the measurements of scattering coefficients hitherto made are all subject to considerable errors, amounting to 10 or 20 per cent. in many cases, and as accurate calculations would require

an enormous expenditure of labour, I have contented myself with a rough calculation. Along the real axis the function F reduces to the function $f(r)$ of the previous investigation, but with x in the place of r, so that the values along this axis are known accurately. I have calculated the values of F for a convenient set of values of r along the radii $\theta = 5°$, $10°$, $15°$, $30°$, $45°$, $60°$, $75°$ and $90°$, and by interpolation determined the points along these radii corresponding to a series of constant values of F. Near the real axis the radii are close enough together to give, with the help of the accurately known values along the real axis itself, a reliable picture of the contour lines. This is the important region of the (x, y) plane, since it corresponds to amounts of damping consistent with the production of moderately sharp spectrum lines. At a distance from the real axis the radii are far apart, and the interpolation becomes uncertain, but this is unimportant, because the damping is so large that the fundamental assumption of § 5, on which the present investigation is based, is no longer accurate enough anyhow; besides such large amounts of damping are quite inadmissible for the part of the X- and γ-ray spectrum, which has been photographed and of which the wave-lengths are known.

14. I give a chart of the scattering function F based on these computations; it does not lay claim to any high degree of accuracy, but the general character of the curves is probably correctly interpreted. The following features are noteworthy :—

There is a high and steep peak at the origin, which corresponds to $F = 1$. There is a continual fall of diminishing steepness along the imaginary axis, which forms the main ridge of the surface. From it ridges branch off laterally near the peak, which descend quickly and curve round, so as to abut on the real axis at the points $x = 4{\cdot}2$, $7{\cdot}6$, and so on. These points are points of contact of the real axis with the contour lines $0{\cdot}075$, $0{\cdot}025$, and so on, and they correspond to the maximum values of the function f discussed in the previous investigation, § 10 and graph of fig. 2. Between the lateral ridges and along the real axis lie hollows, the lowest points of which lie on the real axis itself at the points $x = 3{\cdot}15$, $6{\cdot}3$, $9{\cdot}35$, and so on. These points constitute as it were isolated points of the contour lines $0{\cdot}046$, $0{\cdot}0022$, $0{\cdot}0004$, and so on, and correspond to minima of the function f.

We know that the function f vanishes for infinitely great values of its argument x, and we see from (14), § 11, that the same thing is true of the function F for infinitely great values of z, for the real part of the argument $2\iota z$ of the exponential is $-2y$ and is essentially negative. There is, however, no indication in the chart of *negative* values of F; I have not succeeded in proving from any of the

general expressions (14), or (16), § 11, or (18) or (20), § 12, that negative values are impossible, but at any rate their existence is extremely improbable.

15. The contour line $F = 0 \cdot 45$ is particularly important; it is very nearly a circle of radius $1 \cdot 5$ and accordingly cuts the real axis at right angles where $x = 1 \cdot 5$. All contour lines above this one cut the real axis at obtuse angles with its positive direction, all those below at acute angles except on the positive sides of the hollows already mentioned. As we travel away from the real axis

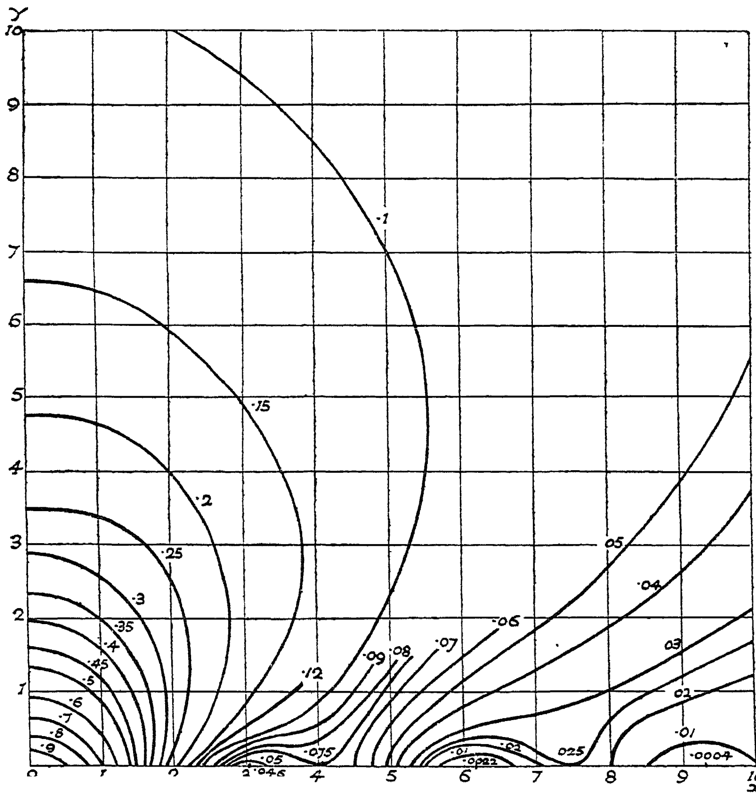

Chart of the Scattering Function F.—The numbers attached to the contour lines denote the corresponding values of F.

in a perpendicular direction starting from points *inside* the circular contour line we *descend*, starting from points *outside* we ascend at first, as we see directly from the chart, but ultimately descend again. The physical interpretation obviously is that for frequencies of the incident radiation less than that corresponding to $x = 1 \cdot 5$, or, by (9), § 10, less than $3c/4\rho \sin (\pi i/n)$, damping of any amount diminishes the scattering, whilst for greater frequencies a small amount of damping increases the scattering, but a large amount diminishes it.

As an example of the numerical values involved let us consider the value $x = 1$, corresponding to the frequency $c/2\rho \sin(\pi i/n)$, or the wave-length $4\pi\rho \sin(\pi i/n)$. The contour line 0·7 for this value of x gives $y = 0{\cdot}08$, which by (17), § 12, corresponds to a logarithmic decrement $l = 0{\cdot}08\,\pi = 0{\cdot}25$; the contour line 0·6 gives $y = 0{\cdot}43$, or $l = 1{\cdot}35$. Thus in this region an increase of the logarithmic decrement equal to 1·1 produces a diminution of one-seventh in the scattering function F. The increased logarithmic decrement means a reduction of amplitude after one vibration to one-fifteenth; for helium, where there is only one function F, the scattering is reduced in the ratio 1·7 to 1·6, that is by about 6 per cent., whilst the corresponding wave-length is $4\pi\rho$, or 3·75 Å.U. with $\rho = 0{\cdot}3$ Å.U., the value given by Bohr's theory. The logarithmic decrement is very far beyond that admissible, which must be very small in this region of the spectrum, but even so the diminution of the scattering is of a much lower order than that observed by Ishino. For rings of several electrons the critical value of the wave-length differs for the different functions F on account of the factor $\sin(\pi i/n)$; it is least for the small values of i, but for these the values of r for a given wave-length and given damping are also least, and the values of F greatest in general, as we see from the chart. Hence the most important terms in the scattering of the ring are just those for which the critical wave-length is least, and which are therefore least likely to be diminished by damping. In view of these considerations we may conclude that damping cannot account for the abnormally low scattering observed by Ishino. This conclusion is rendered practically certain by the very great probability that the scattering function F can never be negative, so that the scattering of an electron ring can never fall below the Simple Pulse Theory's value, $S_1 n$, whilst Ishino's values are only of the order of one quarter of that value.

Magnetic Phenomena in the Region of the South Magnetic Pole.

By C. Chree, Sc.D., LL.D., F.R.S.

(Received May 9, 1923.)

Magnetographs were in operation at Cape Evans, the base station of the British (Terra Nova) Antarctic Expedition (77° 38′ S., 166° 24′ E.), during 1911 and 1912. A second set was in operation at the base station of the Australasian Antarctic Expedition in Adelie Land (67° 0′ S., 140° 40′ E.) during 1912 and 1913. There were synchronous records for seven months, April to October, 1912.

Having been charged with the discussion of both sets of magnetic curves, a unique opportunity was afforded me of studying magnetic phenomena occurring near the south magnetic pole, which is intermediate in position to the two stations. With the approval of Sir Douglas Mawson and of the Committee for the Publication of the Scientific Reports of the British Antarctic (Terra Nova) Expedition, I propose in the present paper to give some of the prominent results of the intercomparison.

The magnetographs at both stations were of the Eschenhagen pattern, primarily intended to record declination (D), horizontal force (H) and vertical force (V). These were the elements actually recorded in Adelie Land, but the instruments at Cape Evans* were modified so as to record two rectangular components of force, described here as N′ and W′, the former inclined 7°·6 east of north, the latter 7°·6 north of west.

The only common element recorded at the two stations was V. Even in temperate latitudes V magnetographs seldom give unmixed satisfaction. The base value and the sensitiveness tend to alter, and there is frequently undue friction. In addition, there is often a large temperature co-efficient. At Cape Evans the temperature was exceptionally steady, and the behaviour of the V magnetograph was unusually good, no sensible change of scale value being observed during the whole of 1912. The Adelie Land V instrument was much less satisfactory, the trace often showing discontinuities suggestive of undue friction.

In high magnetic latitudes it is practically impossible with existing instruments to get satisfactory base value determinations of V curves. The present absolute instrument, whether a dip circle or a dip inductor, measures the

* British Antarctic Expedition, 1910–1913, 'Terrestrial Magnetism,' p. 2.

inclination (I), and the corresponding value of V has to be calculated from absolute observations of I and H through the relation $V = H \tan I$.

In Adelie Land a change of 1′ in I called for a change of 425 γ in V, as against only 20 γ in H. In the highly disturbed conditions prevailing in the Antarctic, and with I determined by a dip circle, the evaluation of the base line value even to the nearest 100 γ presents serious difficulties.

Even in the case of the horizontal components the uncertainties in the base values at both stations were somewhat large. The fact that the absolute instruments at Cape Evans gave D and H, while the elements recorded were N′ and W′, introduced special complications, and it was open to doubt whether local disturbance at both stations did not introduce a small difference between the site of the absolute observations and that of the magnetographs. Fortunately an exact knowledge of absolute values of the elements or of curve base values is not required for the determination of the regular diurnal variation or the absolute daily range, the two quantities dealt with in this paper. So long as the scale values of the curves are known accurately, and the change of the base values in the course of 24 hours is negligible, the absolute value of the element corresponding to the base line is immaterial.

The measurements of the Cape Evans* curves were made at Kew Observatory under my supervision. The Adelie Land* curves were measured in New Zealand. The earlier measurements were made by the observer, Major E. Webb. The later work, which went on during the War, was carried out by Miss Beatrice Smith and some lady assistants, under the general supervision of Prof. Coleridge Farr, of Canterbury College. The tabulated results were transmitted to me in England, and they were followed subsequent to the War by the actual curves.

In both cases, of course, the accuracy of the scale values depended ultimately on the success with which the deflections were made by the Antarctic observers (Dr. Simpson and Captain Wright at Cape Evans, Major Webb in Adelie Land). As all three were trained physicists, deeply interested in their work, we may assume that all reasonable care was taken.

§ 2. The present paper has three principal objects: (i) the comparison of the regular diurnal variation of the magnetic elements from all days at the two stations, (ii) the influence of disturbance on the diurnal variation, and (iii) the best method of classifying days according to disturbance. Magnetic

* In Adelie Land an hourly value represented the mean ordinate for 60 minutes centering at the hour. At Cape Evans it meant the mean of three ordinates measured exactly at the hour, and at 20 minutes before and after.

disturbance in ordinary latitudes is but a feeble echo of that in high latitudes, and the sensitiveness of the regular diurnal variation to disturbance is a special feature of high latitudes. Thus the Antarctic records are specially fitted to throw light on question (iii), which is one of immediate practical interest to all magneticians. Subsidiary to (i) is the question which are the best magnetic elements to record in high magnetic latitudes.

Diurnal inequalities were calculated for both stations from all complete days of each month. Adelie Land (A. L.) inequalities had been got out for Greenwich time as well as local time. For Cape Evans (C. E.) they had been got out for the time of 180° E., so that transformation to Greenwich time was simple. Greenwich time is accordingly employed here throughout. Our object being to elucidate principal features only, inequalities are given in Tables I and II not for the seven individual months, but for two seasons. The first (Wi.), composed of the 4 months May to August, represents winter (in the Antarctic), the second, composed of the three months April, September and October, is described as Equinox (Eq.). If records had existed for March at Adelie Land, it would, of course, have been included. Of the six elements included in Tables I and II, N (component to true north), W (component to true west) and I at both stations, and at Cape Evans also D and H, had their inequalities determined by combining inequalities from two or more of the elements actually recorded. Inequalities so calculated are in one respect less satisfactory than those derived from the curve measurements of a single element. In the latter case an error in scale value affects every hourly inequality figure in the same proportion, so that the type of inequality, times of maximum and minimum, and so on, are quite unaffected. In the case, however, of say, an N inequality—whether derived from N′ and W′ inequalities, as at Cape Evans, or from D and H inequalities, as in Adelie Land—an error of scale value in one of the recorded elements affects the hourly values of the composite element differently, and so affects the type of the inequality.

At Cape Evans the I inequality really depended on the inequalities of three elements N′, W′ and V. But there, and still more in Adelie Land, the influence of changes in V on the I inequality was relatively so small that it would require a serious error in the V scale values to be of importance.

At both stations, as already mentioned, some uncertainty exists as to the possible effects of local disturbance. The force equivalent of a declination change of 1′, for example, depends on the value of H at the site occupied by the magnetograph. If this differs from the value of H at the site where the

absolute observations are made, and this latter value of H is used, the force equivalent deduced is not correct.

§ 3. Tables I and II follow parallel lines. By range is meant the difference between the extreme hourly values, which are distinguished by heavy type. By A. D. (Average Departure) is meant the arithmetic mean of the 24 hourly departures from the mean of the day. The A. D. is less affected than the range by "accidental" irregularities, and is in some ways a better measure of the activity of the forces to which the diurnal inequality is due.

In high latitudes magnetic disturbance is so large and continuous that smooth diurnal inequalities are not to be expected, unless a very large number of months is included. The wonder is not that irregularities occur in the sequence of figures in Tables I and II, but that they are so small.

Comparing corresponding Wi. and Eq. inequalities in Tables I and II, it will be seen that while there is a marked difference in amplitude—ranges and A. D.s being invariably much larger in equinox than in winter—there is little, if any, difference in type or phase between the seasons. This uniformity of type, it may be added, extended to summer.

In view of the similarity of type, graphical representation is confined in fig. 1 to an inequality which represents the arithmetic mean of those for winter and equinox. At both stations the ranges and A. D.s in the summer inequalities were largely in excess of those for the equinoctial. Thus, large as the amplitudes of the inequalities in fig. 1 are, they are considerably smaller than they would have been had the whole year 1912 been represented. 1913 was a year of sunspot minimum, and there was a large fall in the amplitude of Cape Evans inequalities between 1911 and 1912, and also in the amplitude of Adelie Land inequalities between 1912 and 1913. It was thus unfortunately not possible to make a satisfactory estimate at either station of a summer inequality to correspond to the winter and equinoctial inequalities given in Tables I and II.

One of the first things to catch the eye in fig. 1 is the fact that while there is approximate agreement in phase between the D inequalities at the two stations, there is approximate opposition of phase in the case of the H and I inequalities. Adelie Land declination was about 6°·5 west of north, thus the station was situated presumably somewhat west of north of the south magnetic pole. Cape Evans declination was about 155° east of north; thus the station was situated S.S.E. of the magnetic pole. In both cases in Table I increasing declination signifies that the north end of the magnet was moving to the west. Thus fig. 1 shows that, speaking generally, the N. end of the magnet was at any instant moving in the same direction at the two stations;

but this implies that clockwise movement of the *magnet* at the one station usually synchronised with anti-clockwise movement at the other, and con-

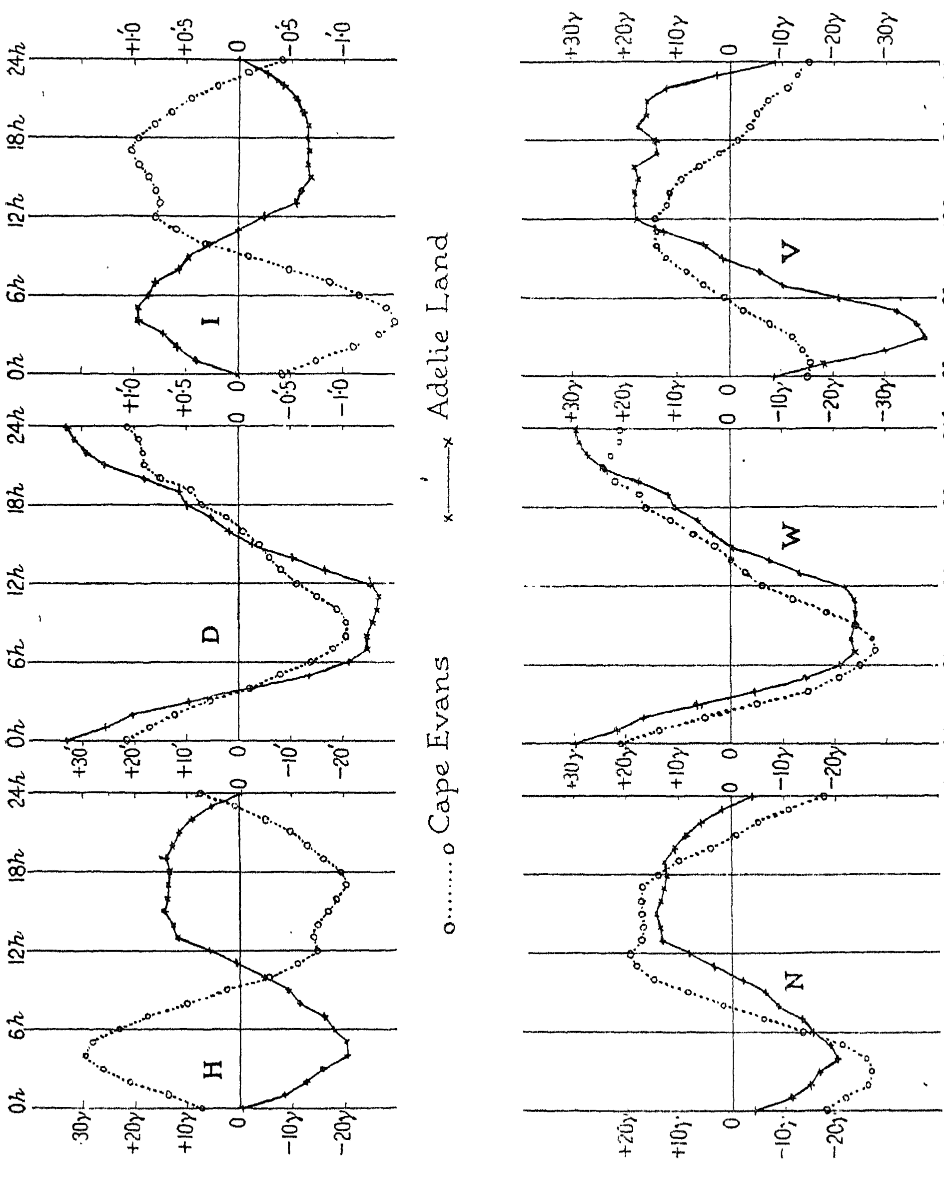

Fig. 1.—Diurnal Inequalities from all Complete Days at Cape Evans and Adelie Land.

versely. The opposition of phase in H at the two stations signifies in a general way that when H increased at the one station it decreased at the other. Similarly the opposition of phase in I implies that increase of dip at the one

station was accompanied by decrease of dip at the other. These phenomena would obviously follow from a daily oscillation in the position of the south magnetic pole. A movement on its part towards the N.W. would diminish H and increase I at Adelie Land, while increasing H and diminishing I at Cape Evans.

Comparing N and W inequality curves for the two stations in fig. 1 we see that they were not exactly in phase, but that the difference in phase is only an hour or two. The difference of longitude between the two stations represents a difference in local time of about 1 hour 43 minutes, Cape Evans being the more easterly and so earlier station. A lag of about $1\frac{3}{4}$ hours in the inequalities at Adelie Land is thus what we should expect, if the position of the station relative to the magnetic pole is immaterial. The amplitudes of the W inequalities at the two stations appear very nearly equal. Cape Evans has decidedly the larger N inequality. Still, as a first approximation, when allowance is made for the difference in local time, the regular diurnal variations of the horizontal magnetic elements at the two stations are not much different. The natural inference is that the exact position, whether north, south, east or west, of stations near the magnetic pole is of minor importance.

In the case of V the lag at Adelie Land seems somewhat in excess of the time equivalent of the difference of longitude. Still, as a first approximation, the changes at the two stations are in phase, when allowance is made for the difference in local time. There is, however, a marked difference in amplitude, the diurnal range at Cape Evans not being more than half that in Adelie Land. If the Adelie Land amplitude had been the smaller, suspicion might have been entertained that the friction, the consequences of which were so often visible in the Adelie Land curves, was partly responsible. But, as it is, assuming no serious error in the scale value at either station, we must suppose that changes in V were habitually much larger in Adelie Land—the station nearer the magnetic pole—than at Cape Evans.

§ 4. Fig. 2 illustrates the diurnal variations, for winter and equinox combined, by the corresponding vector diagrams, the N W diagram in the horizontal plane, the V W diagram in the east-west vertical plane, and the V N diagram in the meridian plane. In all cases each of the four arms of the cross at the origin represents 5γ. The hours 0, 6, &c., shown on the diagrams refer to Greenwich mean time.

The N W vector diagrams are both described anti-clockwise. 12 h. G.M.T., it will be noticed, answers to about 23 h. (11 p.m.) at Cape Evans, and to

21·7 h. at Adelie Land. The Adelie Land diagram is distinctly more elliptical than the Cape Evans diagram. Both curves differ from vector diagrams for British stations in the respect that the area traced by the radius vector during

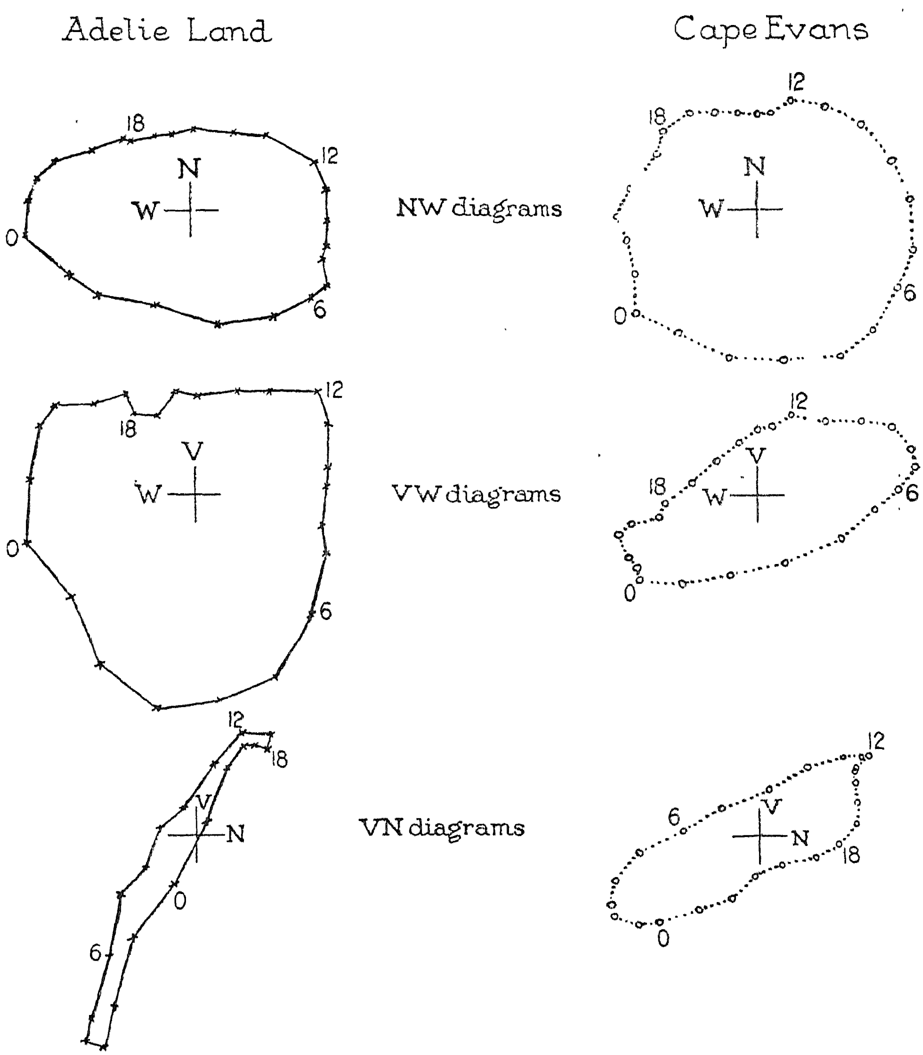

FIG. 2.—Diurnal Inequalities.—Vector Diagrams.

the "night" hours (6 p.m. to 6 a.m. L.M.T.) is but little smaller than that described during the "day" hours. That peculiarity, it may be added, is equally true of Antarctic vector diagrams for winter, equinox and summer. At Cape Evans during nearly the whole of summer the sun never sets, and

during nearly the whole of winter it did not rise. Thus this particular phenomenon was little dependent on the sun's altitude.

The Adelie Land V W diagram, thanks to the much larger range of V, includes a much larger area than the corresponding Cape Evans diagram.

The most outstanding of all the vector diagrams is the V N diagram at Adelie Land. It has an extraordinarily narrow elongated shape, which, it may be added, was characteristic alike of winter, equinox and summer. Both N and V at Adelie Land showed such slow change between 12 h. and 20 h. G.M.T. that hourly values could not be shown on the diagram without making it too confused. Accordingly means were formed for the two groups of hours 13 to 16 and 17 to 19, and these are represented as only two points in the diagram, corresponding respectively to 14·5 h. and 18 h. Several years' results would probably be necessary to show with certainty the normal progression from 12 h. to 20 h. The exact shape of the upper apex of the V N diagram at Adelie Land is thus somewhat indeterminate. The lower apex occurred about 3·5 h. G.M.T., *i.e.*, about 1 p.m. local time.

In view of the wholly exceptional shape of the Adelie Land V N diagram, it is desirable to explain that it is really due to the close similarity of phase between the V and N diurnal inequalities. This obviously would not be affected by any error of scale value in V, however large. N, of course, is a derived element; but the Adelie Land declination, about 6°·5, is so small that the N diurnal inequality is dominated by H, as may be seen on inspection of Table II. Thus the only sensible effect on the V N diagram of scale errors, if any such existed, would be a change in the general slope of the elongated dimension.

Presumably we shall not be far wrong in assuming that the N W vector diagram at a station in the immediate neighbourhood of the south magnetic pole will be similar to the N W diagrams in fig. 2. The sum of the distances of Cape Evans and Adelie Land from the magnetic pole will naturally be somewhat in excess of the distance (roughly 900 miles) between these stations. The values of H at the two stations are approximately 4,300 γ and 3,000 γ respectively. Thus the rate of increase of H as we travel away from the magnetic pole is presumably something like 7·5 γ per mile. We should thus infer that the mean of the daily tracks of the south magnetic pole during the winter and equinoctial months of 1912 was roughly a circle of some 3 miles radius. On occasions of magnetic storms the instantaneous position of the magnetic pole—defined as the locus where H vanishes—must often be dozens of miles, sometimes probably hundreds of miles, from its mean position.

It is obvious from a study of the D, H, N and W curves in fig. 1 that near a magnetic pole there is a simplification in taking N and W as the fundamental elements. It would, moreover, be exceedingly difficult to record D variations satisfactorily at a station very close to a pole. Even at Adelie Land, in the summer months of 1912, D had a range exceeding 5° in one day out of six, and H often differed from its mean value by 5 per cent. or more. Under such circumstances keeping the D trace on the photographic sheet is not easy, and the interpretation of the D and H curves at times of large disturbance presents serious difficulties. If absolute instruments were available giving N and W directly, the advantages of N and W magnetographs in high magnetic latitudes could hardly be disputed. Another absolute instrument urgently wanted for such latitudes is one measuring V directly.

§ 5. Tables III to VI and fig. 3 are primarily intended to show two things :

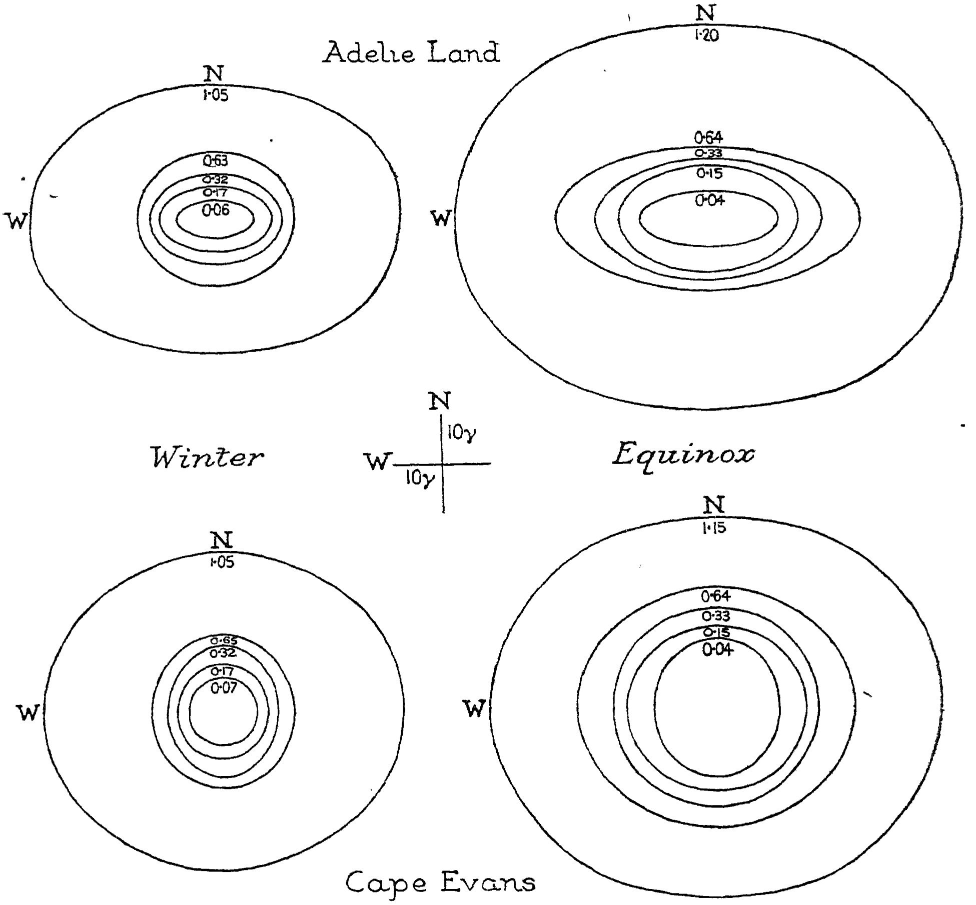

FIG. 3.—N.W. Equivalent Ellipses (for different classes of days, Tables III to VI).

(1) the remarkable sensitiveness of the diurnal inequality in Antarctic regions to the presence of disturbance, (2) the remarkable way in which the international "character" figures got out at De Bilt suffice for the classification of days in the remote Antarctic. The international "character" figures, as is generally known to magneticians, represent the arithmetic means of figures 0 (quiet), 1 (moderately disturbed), and 2 (highly disturbed conditions), assigned daily at a number of magnetic observatories. No one of the few co-operating observatories in the southern hemisphere has a high latitude, thus the application of the international figures to the Antarctic is, from a mathematical point of view, a very extreme case of extrapolation.

Each of the Tables III to VI includes inequalities from the elements actually recorded by the magnetographs, with, in addition, inequalities for the two derived rectangular components N and W. The three first elements in each table, as already explained, have the advantage that mistakes in scale values, if such existed, could not affect any deductions drawn from differences between the several categories of days.

For each element five sets of inequality figures are given. The first is based on the international quiet days selected at De Bilt. The second is derived from the days having international "character" figures 0·1 and 0·2, omitting any which were international quiet days. The third inequality is derived from the days of international characters 0·3 and 0·4, the fourth from the days having international characters from 0·5 to 0·8 inclusive, omitting one or two days which come in the fifth class. The fifth and last inequality comes from the five days of each month having the largest international figures, *i.e.*, the days we may consider the most disturbed days in their respective months according to the international scheme. In the equinoctial tables IV and VI, in the case of the second, third and fourth classes, identically the same days were used for both the stations, and for all the elements. For the winter season, Tables III and V, in these three classes the days used for the two stations were mainly the same, but there were a few exceptions, necessitated by loss of trace on particular days at one or other station. At Cape Evans identically the same days were used for the two horizontal components, except in the fourth class, where one day out of twenty-eight employed for W′ was omitted for N′. In Adelie Land the second and third classes employed identical days for the three elements, with the exception of one day in the third class omitted in D; in the fourth class out of 27 days used for H, three had to be omitted for D and five for V. At both stations the quiet days (first class) were the international quiet days, and the disturbed days (fifth class) the days

of largest international character ; but in a few cases, owing to imperfection of record, days had to be omitted or substitutes found.

Substantially the five classes of days in either season were identical for the two stations, and for the several elements. That this was the case so far as the international figures permit a judgment to be formed, is obvious on comparing the mean " characters " given in the tables for the five classes. In forming the classes, it may be well to add, so long as the records for the day from both stations were complete, the only consideration taken into account was the international " character " figure. Also every day of complete trace was included in one or other of the classes except two or three days of " character " 0·0, which were not international quiet days, and a very few days of " character " greater than 0·8, which did not come amongst the five days of largest " character " figure of the month.

Except in the first and last classes of days in Tables III to VI, the days contributed by the several months differed in number. Even within a four-month season the seasonal change in the regular diurnal inequality is sensible. Thus, in forming the inequalities in the tables, equal weight was allotted to the individual months, not the individual days. In some cases a month contributed only three days to a particular class. Thus the wonder is not that irregularities appear in the several inequalities, but that the results are as smooth as they are. The inequalities derived from the highly disturbed days are not specially erratic.

The inequalities from the different groups of days, it will be seen, are essentially of the same type. Considering the ranges and A. D.s for the winter season in Tables III and V, we observe in every single case an increased amplitude as we pass from a class of lower to a class of higher international " character." The same is true for the equinoctial inequalities in Tables IV and VI with one exception, viz., the case of V for the class with international figures 0·3 or 0·4. This has at both stations a somewhat lower range and A.D. than the class with international figures 0·1 or 0·2. At Cape Evans the amplitude appears low for the class with international figures 0·3 or 0·4, but in Adelie Land it is the amplitude of the class with international figures 0·1 or 0·2 which seems to be exceptionally high.

In view of the comparatively small difference between the mean " character " figures of the first two classes, it is very remarkable that the five international quiet-day class should give in every case the lower range and A.D. It seems a natural inference that whatever the weak points of the present international scheme may be, it at least secures the primary object for which it was designed, the selection of satisfactory international quiet days.

At the other end of the scale, the disturbed day class shows a very large excess both in range and A. D. over the next class. In this case the excess in the mean "character" figure of the disturbed day class is substantial. Still the result is undoubtedly a further tribute to the existing international scheme.

§ 6. If the inequalities for the five classes of days in Tables III to VI were illustrated by ordinary vector diagrams, the irregularities would be apt to divert the eye from the essential features. A new type of diagram is accordingly used to represent the diurnal variation in the horizontal plane. The true W N vector diagram, as fig. 2 shows, has a generally elliptical shape (including the circle as a special form). The new diagram, which may be termed the equivalent ellipse, has for its principal semi-axes $(4/\pi)$ times the A. D. in the W inequality and $(4/\pi)$ times the A. D. in the N inequality. The A. D. of an inequality is the equivalent of the mean ordinate, and the mean ordinate in an ellipse is $(\pi/4)$ times the corresponding semi-axis. If the W inequality is the larger, the equivalent ellipse in fig. 3 is elongated in the horizontal direction. If the N and W inequalities are of like amplitude, the ellipse tends to the circular form.

At Cape Evans in winter the equivalent ellipse is very nearly a circle for the quiet days, and for the next three classes the N axis is slightly the larger. In equinox the W axis is always the larger except for the quiet days. At both seasons the W axis is decidedly the larger for the disturbed days. The tendency would thus seem to be for disturbance to increase the amplitude of the W inequality more than that of the N inequality.

In Adelie Land the W axis is always decidedly the larger; but, relatively considered, its excess is greatest for the quiet days. The shape of the equivalent ellipses at the two stations is much more similar for the disturbed than for the quiet days.

Fig. 3 shows convincingly that the amplitude of the regular diurnal inequality pulses throughout the whole Antarctic as disturbance waxes and wanes. It shows the futility of studying the laws of variation of the diurnal inequality with geographical position unless strictly corresponding material is available from the different stations, especially those in high latitudes.

§ 7. Satisfactory as the existing international scheme is for the selection of quiet and disturbed days, it has the admitted defect that the numerical values 0·0, 0·1, &c., which it provides have a varying significance. They discriminate satisfactorily between the days of a particular month, but not between different months, or season or years. Moreover, the values 0, 1, 2 assigned at individual stations are largely dependent on the idiosyncracies

of the individual. A change of directorate may simulate the immediate sequence of sunspot minimum by sunspot maximum. Various more definite characteristics have been suggested. The first proposal which aroused general interest was that of the late Prof. Bidlingmaier. He suggested the use of a quantity, which he termed the "magnetic activity," representing the mean value for the day of $(1/8\pi)\ (\alpha^2+\beta^2+\gamma^2)$, where α, β, γ are departures of three rectangular components of magnetic force from their mean values. Every one who has tried this scheme has found the amount of work which it entails to be too serious. To meet this objection I have myself proposed the use of $\Delta X^2+\Delta Y^2+\Delta Z^2$, where ΔX, ΔY, ΔZ are the absolute daily ranges of three rectangular force co-ordinates. For example, at Eskdalemuir, where N, W and V are recorded, the criterion proposed is $\Delta N^2+\Delta W^2+\Delta V^2$. If instead of N and W the elements recorded are H and D, the criterion is $\Delta H^2+(H\Delta D)^2+\Delta V^2$, where H is the (approximate) current value of the horizontal force. This criterion has an absolute value independent of the observer, and if otherwise suitable should admit of the inter-comparison of different stations, seasons and years. Absolute daily values, however, of $\Delta N^2+\Delta W^2+\Delta V^2$ would not be convenient for the purposes of a central bureau. Accordingly, at the meeting of the International Union of Geodesy and Geophysics held at Rome in May, 1922, I suggested that stations should contribute not the daily absolute values of $\Delta N^2+\Delta W^2+\Delta V^2$ but the ratios borne by these daily values to their monthly mean value, with in addition the absolute value of the monthly mean. The central bureau would thus have from each station a series of numerical values 0·1, 0·2, &c. Taking the arithmetic mean of the values thus assigned by the different stations for each individual day, it would obtain as at present international figures, which would fix the "character" of each day in the month as less or more disturbed.

At a later stage the mean monthly values of the criterion from the several co-operating stations would serve for the intercomparison of different months, years and stations. A sufficiently approximate absolute value of the criterion for any individual day at a particular station could be deduced, by any one who desired it, from the ratio figure for the day and the absolute mean monthly value. The method of daily ratios is independent of the precise form of the criterion, whether $\Delta X^2+\Delta Y^2+\Delta Z^2$ or $(\Delta X^2+\Delta Y^2+\Delta Z^2)^{\frac{1}{2}}$, or any other function of the absolute daily ranges.

§ 8. Tables VII and VIII apply the method just described to the absolute daily ranges at Eskdalemuir, Cape Evans and Adelie Land for the seven months

April to October, 1912. Table VII deals with the four months, May to August, and Table VIII with the three remaining (equinoctial) months. The data for each month are given in four columns. Under I is the international "character" figure for the day. The daily ratios of the criterion for Eskdalemuir (Esk.), Cape Evans (C. E.) and Adelie Land (A. L.) follow in order in the next three columns. The criterion employed except in July was $\Delta N^2 + \Delta W^2 + \Delta V^2$ for Eskdalemuir, $\Delta N'^2 + \Delta W'^2 + \Delta V^2$ for Cape Evans, and $\Delta H^2 + (H\Delta D)^2 + \Delta V^2$ for Adelie Land. Vertical force data were lacking in July at Eskdalemuir, and the criterion employed for that month was $\Delta N^2 + \Delta W^2$ for Eskdalemuir, $\Delta N'^2 + \Delta W'^2$ for Cape Evans and $\Delta H^2 + (H\Delta D)^2$ for Adelie Land.

When, owing to failure of trace or other cause, range data are lacking for a particular day, that day cannot be taken into account when calculating the absolute mean value of the criterion for the month. If the days for which data are lacking happen to be average days this does not matter. What takes place when the defective day happens to be a day of large disturbance may be seen by considering August 6th, a day for which data were lacking at Cape Evans. Judging by the international figure, the 6th was much the most disturbed day of the month. If we suppose that the disturbance at Cape Evans was similar to what it was in Adelie Land, the mean value of the criterion from all days of the month would have been some 10 per cent. larger than the value actually derived from the 29 days available. The individual values of the ratio for August at Cape Evans in Table VII are thus probably some 10 per cent. higher than they would have been had the record for the month been complete. This would, however, have been absolutely without effect on the relative order of the days when arranged according to disturbance. Deficiencies of this kind are sure to happen occasionally at any observatory provided with only one set of magnetographs. If only a day or two's trace is defective in the course of a month, the consequences will usually be trifling; but if a number of days' trace were lacking, it would probably be best to leave that particular station out of account when calculating the international "character" figures.

In Tables VII and VIII the mean monthly values of the criterion from all the days employed appear in the last line, the unit being $(10\,\gamma)^2$. The monthly mean international "character" figures were 0·45 for July, 0·45 for April, 0·46 for October, 0·49 for August, and 0·47 for the remaining three months, the mean for the equinoctial months combined being 0·46, and so exactly the same as for the four-month group. This represents an exceptionally uniform state of matters. The general features are more easily recognised in sub-

sequent tables which summarise the results, but before leaving Tables VII and VIII a few outstanding cases call for notice.

§ 9. One of the most outstanding cases is that of July 6. The international figure is only 0·7, as compared with 1·2 on the previous day, and in general the 5th was much the more disturbed day of the two. Fourteen co-operating stations assigned a "character" 0 to the 6th, and no single station assigned a 2; while five stations assigned a 2 to the 5th, and only one station a 0. But at Adelie Land the ratios are 3·8 for the 5th and 9·4 for the 6th, the latter value being the largest to be found for Adelie Land during the whole seven months. The cause was a violent but brief storm at Adelie Land on the 6th. Synchronous with this there were visible movements elsewhere, but they were relatively insignificant. These brief highly oscillatory storms of a comparatively local character seem peculiar to high latitudes.

May 29 affords an example of an apparently opposite tendency. The international figure for the day, 0·8, signifies that four stations out of five considered the day slightly disturbed; and in this attitude there was no difference between southern and northern stations. Yet the ratio for the day at Cape Evans is only 0·2, being identical with that for the previous day, the international figure for which is 0·0. This really illustrates a weak point in the use of any ordinary function of the daily range as a criterion. Any one having before him the Cape Evans curves for May 28 and 29 would allow that, so far as the horizontal components of force are concerned, the 28th was unquestionably the quieter day, the greater part of it being in fact exceptionally quiet. But, while the N′ and W′ curves for the 29th were much the more oscillatory, these oscillations hardly affected the daily range; on the other hand, the V range on the 29th was little over half of that for the previous day.

Another weak point in the daily range criterion is illustrated by June 15 and 16. Both days have international figures 0·1, the 15th being one of the international quiet days, and the Adelie Land ratios are also both 0·1; but the entries under Eskdalemuir are respectively 0·8 and 1·0. The days were in reality both quiet at Eskdalemuir, the W traces being on both days particularly smooth; but the ranges, though owing little, if anything, to disturbance, were not small. This is by no means a rare phenomenon in low and mean latitudes.

There are a few cases of marked discrepancy between the ratios for the two Antarctic stations. In most but not all of these, the cause was a relatively high value of ΔV at one of the stations. This accounts for the excess of the C.E. ratio on April 16, and for the excess of the A.L. ratio on May 7, 8, 9 and 17.

In Europe, as is well known, V is often quiet on days when the horizontal components show considerable disturbance. But on other occasions, especially when there are large magnetic storms accompanied by Aurora visible in England, the V trace is as disturbed as the others. There is thus some reason to think that, at least in temperate latitudes, V disturbance is of a more local character than disturbance of the horizontal components. The phenomena just mentioned support this view for the Antarctic.

On some occasions there is rather a striking contrast between the ratios on successive days at the two Antarctic stations. Thus on June 1 the A.L. ratio is treble that for C. E., while on June 2 the C. E. ratio is nearly treble that for A. L. On June 2 ΔV was largest for C. E., while on June 1 ΔV was three times as large at A. L. as at C. E.

An excess in ΔV was not, however, invariably the cause of this phenomenon. On August 22, for example, the C. E. ratio exceeds that for A. L., while on August 23 the A. L. ratio is double that for C. E. In this case a large value in H was mainly responsible for the excess of the A. L. ratio on the 23rd. There are one or two instances of successive days, *e.g.*, September 17 and 18, and October 14 and 15, when the excess of disturbance on the first day suggested by the C. E. and A. L. ratio is much less than that suggested by the Eskdalemuir ratio or the international "character." The highly disturbed conditions seemed more persistent in the high latitudes.

§ 10. Table IX gives final means derived by applying the scheme of characterisation described above. It employs five categories of days defined precisely as in Tables III to VI; but all days are employed, irrespective of whether they are represented at all the stations or not. Even in individual months, as we pass from the first to the fifth class of days, a well marked progressive rise is usually seen in the C. E. and A. L. figures. The method of classification ensures, of course, a regular rise in the international "character" figures. The Eskdalemuir figures, equally with the others, show a large rise as we pass from the fourth to the fifth class of days, but in the lower classes they show a somewhat insufficient sensitiveness to disturbance. Thus, taking the final mean values, in summer there is a rise of only 0·02 in the figure as we pass from the first class to the second, and in equinox a rise of only 0·04 as we pass from the second class to the third.

At Eskdalemuir the difference between the figures for the first and last classes is considerably larger for the equinoctial months than for May to August (summer). This is rather what we should expect, since in Britain the equinoctial months are the most disturbed, and the summer months show

the largest diurnal inequality ranges for quiet-days. At both Antarctic stations, however, the excess of the disturbed-day figure over the quiet-day figure is largest for May to August (winter), which in the Antarctic is the quietest season. The explanation may be that winter is also the season when the Antarctic quiet-day diurnal inequality is smallest.

It has been objected to the second power of the range criterion that it supplies excessively large figures for days of intense magnetic storm. This criticism has more force when we use absolute than when we use relative figures. If we took $1\gamma^2$ as unit, the absolute values of $\Delta N^2 + \Delta W^2 + \Delta V^2$ might run to millions, and be inconvenient to print. When relative figures are used there is not much force in the criticism, and from a physical point of view it appears rather a superficial one. The primary consideration would seem to be whether the criterion gives a fair representation of the varying intensity of disturbance on different days. A first power of the range criterion seems to me to give a very inadequate idea of the difference between quiet and highly disturbed days. It would, I think, probably serve about as well in practice as a second power criterion for the selection of the five most disturbed days of the month; but at the other end of the scale it would, I think, prove less satisfactory. Substituting a first power for a second power criterion would roughly halve the sensitiveness for discriminating between days in our first and second classes. For that purpose our second power criterion seems none too sensitive at Eskdalemuir; and Eskdalemuir, though a very quiet place compared with the Antarctic stations, is one of the most disturbed of the European and Asiatic stations.

§ 11. In preparing Table X the days were arranged in twelve groups according to the size of the international "character" figure, and the mean value of the disturbance criterion was found for each group. Two criteria were employed, the first the same as that employed in Tables VII, VIII and IX, the second differing from it only in the omission of ΔV^2. The unit employed is $(10\gamma)^2$. Results are given separately for the group of months May to August, and for the equinoctial months. There being no V data for July at Eskdalemuir, the summer results for the first criterion at that station depend only on three months. Owing to the small number of highly disturbed days, the days with "characters" 1·0 and 1·1 were combined in one class, and all those with higher "characters" in a second class. An idea of the composition of these two classes may be derived from the corresponding mean international "character" figures which are given in brackets.

Table I.—Declination and Inclination. Diurnal

Element.	Station.	Season.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
			′	′	′	′	′	′	′	′	′	′	′
D.	C.E.	Wi.	+14·9	+11·3	+ 5·5	− 1·3	− 5·4	− 9·9	−15·4	−17·1	−15·8	−13·6	−13·2
	,,	Eq.	+19·8	+13·5	+ 5·4	− 2·7	−10·5	−17·5	−20·9	−24·0	−25·2	−23·8	−17·0
	A.L.	Wi.	+21·8	+15·9	+ 7·0	− 3·3	−12·0	−15·7	−19·0	−17·8	−17·1	−18·8	−21·7
	,,	Eq.	+28·9	+24·4	+11·9	− 1·6	−15·3	−26·8	−30·2	−31·1	−34·4	−34·1	−31·9
I.	C.E.	Wi.	− 0·57	− 0·89	− 1·00	− 1·15	− 1·14	− 0·96	− 0·70	− 0·37	− 0·03	+ 0·26	+ 0·52
	,,	Eq.	− 0·90	− 1·34	− 1·70	− 1·85	− 1·70	− 1·35	− 1·04	− 0·59	− 0·15	+ 0·38	+ 0·68
	A.L.	Wi.	+ 0·44	+ 0·57	+ 0·65	+ 0·73	+ 0·74	+ 0·64	+ 0·64	+ 0·50	+ 0·35	+ 0·18	+ 0·07
	,,	Eq.	+ 0·37	+ 0·61	+ 0·79	+ 1·20	+ 1·18	+ 1·09	+ 0·95	+ 0·65	+ 0·58	+ 0·34	− 0·07

Table II.—Horizontal Force, North, West and Vertical Components.

Element.	Station.	Season.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
			γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
H.	C.E.	Wi.	+10·6	+17·1	+19·3	+22·6	+22·7	+19·4	+14·3	+ 7·9	+ 1·2	− 4·5	− 9·6
	,,	Eq.	+16·7	+25·5	+32·8	+36·2	+33·4	+26·7	+20·9	+12·2	+ 3·7	− 6·6	−12·5
	A.L.	Wi.	− 9·5	−12·4	−14·0	−15·6	−15·7	−13·4	−13·1	−10·2	− 7·0	− 3·4	− 1·0
	,,	Eq.	− 8·0	−13·4	−17·6	−25·5	−24·9	−22·7	−19·2	−12·9	−11·3	− 6·3	+ 2·2
N.	C.E.	Wi.	−17·4	−21·4	−20·4	−19·7	−17·6	−12·2	− 4·8	+ 1·9	+ 7·3	+11·2	+15·7
	,,	Eq.	−25·6	−30·2	−32·5	−31·3	−24·6	−14·8	− 8·7	+ 1·8	+10·0	+18·6	+20·4
	A.L.	Wi.	−11·6	−13·9	−14·6	−15·0	−14·2	−11·5	−11·0	− 8·1	− 5·1	− 1·4	+ 1·4
	,,	Eq.	−11·0	−15·9	−18·7	−25·1	−23·1	−19·7	−15·9	− 9·5	− 7·6	− 2·6	+ 5·6
W.	C.E.	Wi.	+12·1	+ 5·4	− 2·1	−11·1	−15·7	−19·4	−23·4	−22·5	−18·2	−18·3	−10·7
	,,	Eq.	+15·0	+ 4·2	− 8·0	−18·5	−26·1	−31·0	−32·4	−32·1	−29·8	−23·9	−13·7
	A.L.	Wi.	+18·4	+12·8	+ 4·6	− 4·8	−12·6	−15·6	−18·6	−17·1	−16·2	−17·2	−19·6
	,,	Eq.	+25·0	+20·3	+ 8·6	− 4·4	−16·6	−26·7	−29·3	−29·4	−32·1	−31·3	−28·3
V.	C.E.	Wi.	−11·5	−10·5	− 8·0	− 4·9	+ 1·1	+ 3·6	+ 5·9	+ 9·1	+11·4	+12·1	+ 9·8
	,,	Eq.	−19·5	−17·9	−15·9	−10·3	− 6·4	− 1·7	+ 3·9	+ 7·5	+12·9	+15·2	+17·6
	A.L.	Wi.	−18·9	−27·4	−28·3	−28·5	−25·7	−16·3	−10·8	− 6·7	− 1·6	+ 1·7	+ 8·2
	,,	Eq.	−17·4	−32·6	−46·8	−43·8	−38·7	−25·6	− 9·9	− 4·7	+ 4·3	+ 8·0	+16·8

Table III.—Cape Evans Diurnal Inequalities.

Element.	Mean Character of class.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
		γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
N′	0·07	− 8·3	−10·6	− 9·1	− 9·9	− 7·6	− 4·3	− 1·1	+ 2·6	+ 7·2	+ 5·7	+ 6·3
	0·17	−11·7	−14·7	−13·6	−11·0	− 8·7	− 7·5	− 2·2	+ 3·5	+ 9·0	+ 8·7	+ 8·7
	0·32	−18·3	−18·1	−16·1	−19·5	−11·7	− 5·7	− 2·6	+ 4·3	+ 5·6	+10·0	+15·9
	0·65	−21·1	−18·0	−18·1	−17·4	−15·6	−11·9	− 8·1	− 1·9	+ 2·3	+ 9·3	+21·3
	1·05	−38·2	−52·0	−45·2	−37·0	−31·2	−18·9	+ 3·4	+15·1	+22·7	+30·9	+35·0
W′	0·07	+ 2·7	+ 1·1	− 3·1	− 7·2	− 8·4	−11·1	−10·9	− 8·6	− 8·1	− 3·7	− 2·9
	0·17	+ 7·5	+ 3·2	− 3·1	− 7·7	−13·0	−14·7	−15·8	−12·4	−12·4	− 5·4	− 4·0
	0·32	+ 7·7	+ 3·1	− 5·5	− 9·2	−12·1	−13·2	−16·1	−14·4	−11·7	− 9·2	− 6·6
	0·65	+ 9·3	+ 3·3	− 2·3	− 6·3	−12·0	−18·6	−23·8	−21·7	−15·7	−16·0	−13·2
	1·05	+25·0	+ 5·3	−10·9	−35·1	−39·4	−48·3	−53·4	−55·7	−41·7	−26·9	−20·2
V	0·07	− 6·5	− 5·4	− 4·3	− 1·9	− 0·1	+ 1·6	+ 4·0	+ 4·2	+ 5·3	+ 5·5	+ 4·2
	0·17	− 7·7	− 7·7	− 6·9	− 4·3	− 1·0	+ 3·0	+ 6·0	+ 6·1	+ 7·1	+ 5·6	+ 4·7
	0·32	− 9·8	− 8·6	− 7·6	− 0·7	0·0	− 0·2	+ 2·8	+ 3·9	+ 5·9	+ 5·6	+ 8·9
	0·65	−11·9	−11·9	− 9·0	− 6·2	− 3·0	− 0·4	+ 4·4	+ 7·6	+10·7	+10·9	+10·0
	1·05	−20·7	−18·7	−14·7	−11·8	+ 0·2	+ 8·4	+ 7·9	+19·7	+28·5	+34·2	+22·9
N	0·07	− 7·9	−10·3	− 9·4	−10·8	− 8·6	− 5·7	− 2·5	+ 1·4	+ 6·1	+ 5·2	+ 5·0
	0·17	−10·6	−14·2	−13·9	−11·9	−10·3	− 9·4	− 4·3	+ 1·8	+ 7·3	+ 7·0	+ 8·1
	0·32	−17·1	−17·5	−16·7	−20·5	−13·2	− 7·4	− 4·7	+ 2·4	+ 4·0	+ 8·7	+14·9
	0·65	−19·7	−17·4	−18·2	−18·1	−17·0	−14·2	−11·2	− 4·7	+ 0·2	+ 7·1	+19·4
	1·05	−34·6	−50·8	−46·2	−41·3	−30·1	−25·1	− 3·7	+ 7·6	+17·0	+27·1	+32·0
W	0·07	+ 3·8	+ 2·5	− 1·9	− 5·8	− 7·3	−10·4	−10·7	− 8·9	− 9·0	− 4·4	− 3·7
	0·17	+ 9·0	+ 5·1	− 1·3	− 6·2	−11·7	−13·6	−15·4	−12·8	−13·5	− 6·5	− 5·1
	0·32	+10·1	+ 5·5	− 3·3	− 6·6	−10·4	−12·3	−15·6	−14·8	−12·3	−10·4	− 8·6
	0·65	+12·0	+ 5·6	+ 0·1	− 3·9	− 9·8	−16·9	−22·5	−21·2	−15·9	−17·1	−15·9
	1·05	+29·8	+12·1	− 4·8	−29·9	−35·9	−45·4	−53·4	−57·2	−44·3	−30·7	−24·6

Inequalities from all complete days (G.M.T.).

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range.	A.D.
′	′	′	′	′	′	′	′	′	′	′	′	′	′	′
−10·0	− 6·6	− 4·9	− 3·1	− 1·0	+ 0·5	+ 5·3	+ 6·8	+12·0	+13·0	+14·6	+15·6	+17·8	34·9	9·8
−12·4	− 9·3	− 6·8	− 4·3	− 0·5	+ 4·4	+ 8·6	+11·8	+17·6	+23·5	+22·2	+23·0	+25·0	50·2	14·6
−21·0	−15·9	−10·6	− 4·0	+ 0·4	+ 2·9	+ 6·6	+ 8·7	+15·8	+21·0	+23·8	+26·6	+26·4	48·3	14·7
−29·7	−17·3	−10·0	− 1·1	+ 3·4	+ 7·4	+13·0	+14·0	+20·1	+30·0	+34·5	+36·2	+39·4	73·8	22·0
+ 0·72	+ 0·60	+ 0·65	+ 0·71	+ 0·73	+ 0·72	+ 0·78	+ 0·60	+ 0·48	+ 0·29	− 0·17	− 0·04	− 0·39	1·93	0·60
+ 0·86	+ 0·91	+ 0·93	+ 1·03	+ 1·19	+ 1·34	+ 1·17	+ 1·01	+ 0·80	+ 0·63	+ 0·25	− 0·12	− 0·45	3·19	0·93
− 0·18	− 0·42	− 0·56	− 0·59	− 0·60	− 0·54	− 0·56	− 0·59	− 0·57	− 0·35	− 0·37	− 0·20	+ 0·10	1·34	0·47
− 0·29	− 0·68	− 0·65	− 0·78	− 0·72	− 0·80	− 0·75	− 0·76	− 0·65	− 0·65	− 0·49	− 0·33	− 0·09	2·00	0·65

Diurnal Inequalities from all complete days (G.M.T.).

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range.	A.D.
γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
−13·6	−11·4	−12·5	−13·7	−14·2	−14·2	−15·7	−12·3	−10·0	− 6·3	− 4·1	+0·1	+ 6·9	38·4	11·8
−16·1	−17·2	−17·6	−19·8	−23·1	−26·5	−23·2	−20·2	−16·1	−12·9	− 5·6	+ 1·5	+ 7·9	62·7	18·1
+ 4·3	+ 9·1	+11·8	+12·5	+12·6	+11·1	+11·6	+12·2	+11·7	+ 9·4	+ 7·7	+ 3·9	− 2·6	28·3	9·8
+ 6·7	+14·2	+13·5	+16·0	+15·0	+16·4	+15·5	+15·9	+13·7	+13·6	+10·2	+ 6·7	+ 1·6	41·9	13·5
+17·6	+13·8	+13·9	+14·0	+13·4	+12·6	+11·4	+ 7·5	+ 2·7	− 1·2	− 4·0	− 8·4	−15·7	39·0	11·9
+21·2	+20·5	+19·6	+20·2	+21·1	+21·6	+16·4	+12·0	+ 5·2	− 0·8	− 6·7	−13·6	−20·4	54·1	17·4
+ 6·5	+10·7	+12·7	+12·8	+12·5	+10·6	+10·7	+11·1	+ 9·8	+ 7·0	+ 5·0	+ 0·9	− 5·3	27·8	9·3
+ 9·8	+15·9	+14·5	+16·0	+14·5	+15·5	+14·0	+14·3	+11·5	+10·3	+ 6·5	+ 2·8	− 2·6	41·1	12·6
− 5·4	− 2·5	− 0·1	+ 2·4	+ 4·9	+ 6·7	+12·6	+12·8	+17·7	+17·2	+18·1	+17·4	+17·0	41·5	12·0
− 7·0	− 3·0	− 0·1	+ 3·7	+ 9·4	+16·3	+19·6	+21·9	+26·6	+31·8	+27·2	+25·1	+24·6	64·2	18·8
−18·3	−13·2	− 8·1	− 2·1	+ 1·8	+ 3·9	+ 7·3	+ 9·2	+15·5	+19·9	+22·2	+24·3	+23·4	43·9	13·6
−25·8	−13·8	− 7·4	+ 0·9	+ 4·8	+ 8·6	+13·5	+14·4	+19·6	+28·5	+32·1	+33·2	+35·5	67·6	20·4
+11·3	+ 8·7	+ 8·2	+ 7·0	+ 4·0	+ 0·4	− 2·5	− 5·2	− 6·8	− 8·9	−10·1	−11·9	−12·3	24·4	7·7
+17·1	+15·1	+14·8	+11·9	+ 7·4	+ 3·8	− 0·5	− 2·5	− 3·8	− 5·6	−11·2	−13·6	−18·1	37·1	10·6
+14·8	+17·1	+18·8	+21·5	+19·5	+12·0	+13·0	+14·9	+12·9	+12·0	+ 9·4	+ 0·5	−12·1	50·0	14·7
+21·2	+18·9	+17·4	+13·1	+16·8	+15·5	+15·4	+20·4	+18·7	+19·3	+14·5	+ 4·3	− 5·2	68·0	18·7

Winter, 1912 (G.M.T.).

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range	A.D.
γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
+ 6·1	+ 5·5	+ 4·5	+ 4·9	+ 5·3	+ 5·2	+ 6·6	+ 3·4	+ 0·8	− 1·3	− 2·6	− 4·2	− 5·4	17·8	5·4
+12·1	+ 8·8	+ 7·9	+ 8·1	+ 7·9	+ 6·7	+ 6·1	+ 3·8	+ 0·4	− 2·8	− 3·7	− 5·8	−10·0	26·8	7·6
+13·8	+13·0	+13·6	+12·5	+ 9·7	+12·0	+ 9·6	+ 6·3	+ 0·5	− 3·1	− 6·1	−11·6	−15·2	35·4	10·6
+21·6	+15·7	+14·4	+13·9	+16·5	+14·3	+10·6	+ 7·3	+ 1·0	− 1·3	− 6·7	− 9·8	−18·1	42·7	12·3
+39·3	+28·6	+31·1	+30·1	+26·9	+22·2	+20·2	+ 8·0	− 1·2	−11·8	−13·7	−22·0	−42·6	91·3	26·1
− 1·3	+ 1·0	+ 2·2	+ 2·2	+ 3·5	+ 3·9	+ 6·4	+ 6·9	+ 8·5	+ 7·0	+ 7·7	+ 7·7	+ 4·5	19·6	5·4
0·0	+ 1·8	+ 1·9	+ 4·2	+ 4·3	+ 5·7	+ 6·8	+ 6·7	+10·0	+ 9·5	+ 9·8	+ 8·7	+ 7·7	25·8	7·3
− 3·3	− 1·4	+ 0·4	+ 1·8	+ 2·6	+ 5·7	+13·6	+13·0	+11·6	+10·7	+ 9·1	+12·5	+11·3	29·7	8·6
− 7·3	− 2·0	+ 0·9	+ 1·5	+ 9·1	+ 8·3	+16·0	+12·7	+15·5	+15·5	+16·4	+16·8	+13·6	40·6	11·6
− 4·1	− 4·9	+ 3·6	+10·9	+14·1	+17·3	+29·3	+33·0	+42·6	+42·9	+44·3	+35·8	+36·9	100·0	28·4
+ 3·9	+ 4·0	+ 2·8	+ 3·4	+ 2·4	+ 1·6	+ 0·1	− 1·7	− 2·7	− 3·7	− 4·8	− 6·8	− 5·7	12·3	3·6
+ 5·4	+ 6·3	+ 5·3	+ 5·6	+ 4·0	+ 1·8	− 0·4	− 1·9	− 3·1	− 7·0	− 5·8	− 7·5	− 8·1	15·2	5·1
+10·0	+ 9·1	+ 9·8	+ 8·9	+ 5·6	+ 2·3	− 1·2	− 3·2	− 4·4	− 7·3	− 9·1	−10·4	−11·2	21·2	6·1
+15·6	+13·0	+10·3	+ 8·9	+ 4·4	0·0	− 1·2	− 4·3	− 6·3	− 8·2	− 9·7	−11·5	−12·2	27·8	8·0
+27·0	+14·4	+16·8	+10·1	+ 5·7	− 0·9	− 8·3	−14·2	−17·2	−20·0	−22·0	−23·1	−24·2	58·4	16·3
+ 5·9	+ 5·6	+ 4·8	+ 5·2	+ 5·7	+ 5·7	+ 7·4	+ 4·3	+ 1·9	− 0·4	− 1·6	− 3·1	− 4·8	18·2	5·4
+12·0	+ 9·0	+ 8·1	+ 8·6	+ 8·4	+ 7·4	+ 7·0	+ 4·6	+ 1·7	− 1·5	− 2·4	− 4·6	− 8·9	26·2	7·7
+13·2	+12·7	+13·5	+12·6	+10·0	+12·6	+11·3	+ 8·0	+ 2·0	− 1·7	− 4·8	− 9·9	−13·6	35·4	10·5
+20·4	+15·3	+14·4	+14·0	+17·5	+15·3	+12·6	+ 8·9	+ 3·0	+ 0·8	− 4·5	− 7·5	−16·1	40·1	12·4
+38·4	+27·7	+31·3	+31·3	+28·5	+24·3	+23·9	+12·3	+ 4·4	− 6·0	− 7·7	−17·1	−37·3	89·2	25·5
− 2·1	+ 0·3	+ 1·6	+ 1·5	+ 2·8	+ 3·2	+ 5·5	+ 6·4	+ 8·3	+ 7·1	+ 8·0	+ 8·2	+ 5·2	19·0	5·4
− 1·6	+ 0·6	+ 0·8	+ 3·1	+ 3·2	+ 4·8	+ 5·9	+ 6·1	+ 9·9	+ 9·8	+10·2	+ 9·4	+ 9·0	25·6	7·3
− 5·1	− 3·1	− 1·4	+ 0·1	+ 1·3	+ 4·1	+12·2	+12·0	+11·4	+11·0	+ 9·8	+13·9	+13·2	29·5	8·7
−10·1	− 4·0	− 1·0	− 0·3	+ 6·8	+ 6·3	+14·5	+11·6	+15·2	+15·5	+17·1	+17·9	+15·9	40·4	11·6
− 9·2	− 8·6	− 0·5	+ 6·8	+10·4	+14·2	+26·4	+31·6	+42·4	+44·1	+45·7	+38·4	+42·2	102·9	28·7

Table IV.—Cape Evans Diurnal

Element.	Mean Character of class.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
		γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
N′.	0·04	−21·2	−21·4	−21·7	−15·8	− 9·6	− 4·4	− 1·2	+ 4·4	+10·8	+12·2	+13·5
	0·15	−19·7	**−23·1**	−22·1	−17·6	−13·6	− 8·1	− 5·4	+ 6·0	+ 9·3	+16·5	**+18·0**
	0·33	−29·4	**−30·8**	−28·9	−21·3	−19·4	− 8·2	+ 1·2	+ 8·6	+14·8	+16·5	+16·7
	0·64	−25·7	−35·8	**−38·7**	−30·7	−23·2	− 7·5	− 3·2	+ 8·1	+13·9	**+27·8**	+25·6
	1·15	−31·1	−46·4	−51·1	**−66·1**	−52·3	−31·9	− 8·3	+ 7·6	+24·2	+32·7	**+54·9**
W′.	0·04	+ 6·5	− 1·8	− 8·6	−16·2	−17·9	**−18·5**	−17·0	−15·9	−12·9	− 8·6	− 4·5
	0·15	+ 6·3	− 0·4	− 6·9	−15·0	−21·4	**−25·0**	−25·0	−22·2	−20·0	−15·6	− 9·9
	0·33	+ 9·6	+ 0·2	−13·3	−25·3	−32·1	**−32·5**	−26·6	−22·9	−19·3	−14·5	− 6·9
	0·64	+ 9·2	−12·7	−16·1	−23·5	−37·2	**−41·0**	−35·9	−34·0	−31·7	−23·6	−11·5
	1·15	+22·9	+ 9·1	−16·3	−40·1	−46·9	−55·7	−72·3	**−78·0**	−60·9	−36·7	−22·8
V.	0·04	**−16·5**	−14·0	−12·4	− 8·6	− 5·7	− 1·0	+ 2·0	+ 6·5	+ 9·3	+10·3	+ 9·9
	0·15	**−19·0**	−18·9	−15·5	−11·6	− 9·6	− 2·6	+ 2·9	+ 3·9	+ 7·2	+10·8	+11·9
	0·33	**−17·5**	−14·3	−12·2	− 6·2	− 3·1	+ 3·1	+ 5·6	+ 6·3	+ 8·6	+11·1	+11·1
	0·64	**−21·9**	−20·8	−17·5	−11·8	− 7·1	− 2·3	+ 3·7	+ 8·2	+13·2	+17·5	**+21·8**
	1·14	−25·7	**−28·3**	−28·3	−18·4	−10·4	− 6·2	+ 3·3	+11·8	+27·5	+29·0	+31·1
N.	0·04	−20·2	−21·5	**−22·6**	−17·8	−11·9	− 6·8	− 3·4	+ 2·3	+ 9·0	+11·0	+12·8
	0·15	−18·7	**−22·9**	−22·8	−19·4	−16·3	−11·3	− 8·6	+ 3·0	+ 6·6	+14·3	+16·5
	0·33	−27·9	**−30·5**	−30·4	−24·5	−23·5	−12·4	− 2·3	+ 5·5	+12·1	+14·4	+15·6
	0·64	−24·3	−37·2	**−40·5**	−33·5	−27·9	−12·8	− 7·9	+ 3·5	+ 9·6	**+24·4**	+23·9
	1·15	−27·8	−44·8	−52·8	**−70·8**	−58·0	−39·0	−17·8	− 2·8	+15·9	+27·6	+51·4
W.	0·04	+ 9·2	+ 1·0	− 5·7	−14·0	−16·5	**−17·8**	−16·7	−16·3	−14·2	−10·1	− 6·2
	0·15	+ 8·8	+ 2·6	− 3·9	−12·6	−19·4	−23·7	**−24·1**	−22·8	−21·0	−17·6	−12·2
	0·33	+13·4	+ 4·3	− 9·4	−22·3	−29·3	**−31·1**	−26·5	−23·8	−21·1	−16·6	− 9·0
	0·64	+12·5	− 7·9	−10·9	−19·2	−33·8	**−39·6**	−35·2	−34·8	−33·2	−27·1	−14·8
	1·15	+26·8	+15·1	− 9·4	−31·0	−39·6	−51·0	−70·6	**−78·3**	−63·5	−40·7	−29·8

Table V.—Adelie Land Diurnal Inequalities.

Element.	Mean. Character of class.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
		′	′	′	′	′	′	′	′	′	′	′
D.	0·06	+12·2	+ 6·7	+ 2·7	− 5·5	− 9·9	− 9·2	**−11·1**	− 8·3	− 7·9	− 7·5	− 6·1
	0·17	+15·0	+ 9·6	+ 1·0	− 7·4	−11·6	**−14·0**	−13·1	−11·3	−10·1	− 8·7	−10·8
	0·32	+18·4	+14·6	+ 6·5	− 2·6	−12·5	−11·1	−11·0	−11·5	−11·1	−12·8	**−18·7**
	0·63	+24·1	+14·2	+ 9·7	+ 2·0	− 6·3	−13·5	−15·2	−11·0	−12·7	−19·3	**−26·0**
	1·05	+40·2	+37·5	+14·1	− 0·6	−16·8	−28·7	−40·3	−44·2	−40·5	−43·7	**−48·4**
		γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
H.	0·06	− 3·0	− 2·0	− 5·2	− 3·2	− 3·7	− 5·0	**− 6·6**	− 3·2	− 2·8	− 2·3	− 2·0
	0·17	− 5·5	**− 9·2**	− 7·9	− 7·9	− 7·6	**− 9·2**	− 9·1	− 4·7	− 2·2	− 0·2	− 1·0
	0·32	− 6·6	−10·0	− 9·6	−12·0	**−12·6**	−10·9	− 8·0	− 5·4	− 5·3	− 4·5	− 5·6
	0·63	− 8·5	−11·2	−16·4	−17·1	−15·7	−15·5	**−19·2**	−11·8	− 8·2	− 4·3	− 2·6
	1·05	−22·0	−31·2	−27·7	**−36·5**	−33·7	−26·0	−23·3	−27·4	−19·0	− 7·5	+ 4·4
V.	0·06	− 7·6	−16·5	−19·2	**−19·6**	−16·1	− 9·2	− 3·0	− 1·7	+ 0·1	+ 2·6	+ 2·6
	0·17	−12·2	−23·1	**−27·3**	−27·1	−21·4	−12·7	− 8·3	− 0·8	− 1·3	+ 2·7	+ 2·8
	0·32	−21·6	−24·6	−26·0	**−28·8**	−25·6	−18·3	−10·5	− 7·4	− 4·5	− 2·8	+ 7·7
	0·64	−21·2	−26·9	**−33·1**	−32·2	−24·3	−18·1	−15·0	− 7·3	− 2·6	− 2·7	+ 4·2
	1·08	−37·8	**−44·3**	−40·5	−38·7	−39·1	−25·3	−19·4	−16·4	− 1·8	+ 7·5	+26·2
N.	0·06	− 4·3	− 2·7	**− 5·4**	− 2·6	− 2·6	− 4·0	− 5·4	− 2·3	− 1·9	− 1·5	− 1·3
	0·17	− 7·0	**−10·2**	− 8·0	− 7·1	− 6·3	− 7·7	− 7·6	− 3·5	− 1·1	+ 0·7	+ 0·2
	0·32	− 8·5	−11·5	−10·2	**−11·6**	−11·2	− 9·6	− 6·8	− 4·1	− 4·1	− 3·1	− 3·6
	0·63	−11·0	−12·6	−17·3	−17·2	−14·9	−14·0	**−17·5**	−10·6	− 6·8	− 2·2	+ 0·2
	1·05	−26·1	−35·0	−29·0	**−35·6**	−31·7	−22·8	−18·9	−22·5	−14·6	− 2·8	+ 9·5
W.	0·06	+10·6	+ 5·8	+ 1·8	− 5·3	− 9·3	− 8·8	**−10·7**	− 7·8	− 7·4	− 7·0	− 5·7
	0·17	+12·8	+ 7·5	0·0	− 7·6	−11·3	**−13·6**	−12·8	−10·7	− 9·3	− 7·8	− 9·8
	0·32	+15·7	+11·9	+ 4·7	− 3·7	−12·7	−11·2	−10·8	−10·9	−10·6	−12·0	**−17·4**
	0·63	+20·6	+11·4	+ 6·7	− 0·2	− 7·5	−13·9	−15·9	−11·3	−12·3	−17·8	**−23·6**
	1·05	+33·4	+29·9	+ 9·4	− 4·9	−19·0	−28·8	−38·9	**−42·8**	−38·5	−40·0	**−42·8**

Inequalities. Equinox, 1912. G.M.T.

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range.	A.D.
γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
+12·8	+13·8	**+14·4**	+14·0	+12·2	+12·4	+ 7·2	+ 3·5	+ 0·6	− 2·1	− 7·1	−10·8	−16·7	36·1	**11·0**
+17·0	+17·1	+15·7	+13·3	+16·9	+17·3	+10·3	+ 3·8	− 1·4	− 4·9	−11·2	−16·3	−18·0	41·1	**13·4**
+20·7	+16·3	+18·2	+14·9	+16·5	+17·1	+13·1	+ 8·2	+ 2·7	− 2·5	− 9·0	−12·4	−23·4	51·5	**15·5**
+24·4	+19·4	+17·0	+20·6	+19·5	+19·8	+15·5	+14·8	+ 2·0	− 9·1	−14·2	−15·8	−24·1	66·5	**19·0**
+53·5	+35·9	+29·9	+32·9	+26·1	+27·1	+18·7	+12·9	+ 4·2	− 9·9	−14·3	−21·2	−27·6	121·0	**30·0**
− 2·8	+ 2·7	+ 3·5	+ 4·8	+ 6·3	+ 7·6	+ 9·7	+ 9·8	+10·1	+15·1	**+18·0**	+15·5	+15·0	36·5	**10·4**
− 7·4	− 2·5	+ 4·5	+ 4·7	+ 6·2	+11·2	+17·7	+15·8	+16·0	+21·3	**+27·8**	+23·0	+16·6	52·8	**14·3**
− 2·8	+ 1·0	+ 2·5	+ 8·3	+ 9·6	+17·2	+18·2	+23·4	+25·2	**+27·9**	+22·8	+15·2	+15·0	60·4	**16·4**
− 2·4	+ 0·3	+ 3·0	+ 7·3	+12·5	+20·0	+25·7	+32·4	+30·9	+37·4	**+37·8**	+29·2	+24·0	78·8	**22·5**
− 7·0	− 0·2	+ 9·5	+12·6	+23·2	+36·7	+48·8	+45·4	+51·1	**+55·8**	+48·8	+38·0	+35·0	133·8	**36·4**
+10·3	+ 9·8	+10·2	**+10·7**	+ 7·6	+ 4·6	+ 2·6	+ 0·3	− 2·1	− 3·0	− 6·0	−10·3	−14·8	27·2	**7·8**
+11·7	+13·2	**+14·0**	+11·3	+10·5	+ 9·7	+ 3·4	− 0·6	+ 0·6	− 0·1	− 6·0	−13·2	−13·6	33·0	**9·2**
+11·9	+12·1	**+13·1**	+12·8	+ 8·3	+ 4·6	+ 1·8	− 0·6	− 1·6	− 7·9	−15·0	−15·7	−16·2	30·6	**9·2**
+20·4	+19·7	+16·4	+14·3	+ 8·7	+ 5·1	+ 0·1	− 6·9	− 9·6	− 5·9	−13·2	−10·6	−21·3	43·7	**12·4**
+32·5	+24·8	+21·5	+13·8	+ 4·1	− 1·6	− 4·5	− 0·5	− 6·8	−11·2	−16·7	−16·1	−24·3	60·8	**16·6**
+12·3	+14·0	**+14·7**	+14·5	+12·9	+13·3	+ 8·4	+ 4·8	+ 1·9	− 0·1	− 4·7	− 8·6	−14·6	37·3	**11·0**
+15·9	+16·6	+16·1	+13·8	+17·6	**+18·6**	+12·5	+ 5·9	+ 0·7	− 2·0	− 7·4	−13·1	−15·7	41·5	**13·2**
+20·1	+16·3	+18·4	+15·9	+17·6	+19·2	+15·3	+11·2	+ 6·0	+ 1·2	− 5·9	−10·3	−21·2	50·6	**15·7**
+23·9	+19·3	+17·2	+21·4	+21·0	+22·3	+18·8	+18·9	+ 6·1	− 4·1	− 9·1	−11·8	−20·7	64·9	**19·2**
+52·1	+35·6	+30·9	+34·3	+28·9	+31·7	+25·0	+18·8	+10·9	− 2·4	− 7·7	−16·0	−22·7	122·9	**30·2**
− 4·5	+ 0·9	+ 1·6	+ 2·9	+ 4·6	+ 5·9	+ 8·7	+ 9·3	+ 9·9	+15·2	**+18·8**	+16·8	+17·1	36·6	**10·2**
− 9·6	− 4·7	+ 2·4	+ 2·9	+ 3·9	+ 8·8	+16·2	+15·2	+16·0	+21·8	**+29·0**	+24·9	+18·8	53·1	**14·3**
− 5·5	− 1·2	+ 0·1	+ 6·3	+ 7·3	+14·8	+16·3	+22·1	+24·6	**+28·0**	+23·8	+16·7	+18·0	59·1	**16·3**
− 5·6	− 2·3	+ 0·7	+ 4·5	+ 9·8	+17·2	+23·4	+30·2	+30·4	+38·3	**+39·3**	+31·0	+27·0	78·9	**22·0**
−14·0	− 4·9	+ 5·5	+ 8·2	+19·5	+32·8	+45·9	+43·3	+50·1	**+56·6**	+50·2	+40·5	+38·3	134·9	**36·1**

Winter, 1912. G.M.T.

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range.	A.D.
′	′	′	′	′	′	′	′	′	′	′	′	′	′	′
− 5·8	− 6·0	− 3·4	− 0·3	+ 1·0	+ 3·6	+ 3·4	+ 4·0	+10·0	+ 7·0	+ 9·0	+10·8	+10·6	23·3	6·8
−13·1	−11·3	− 4·8	− 2·2	+ 4·2	+ 6·6	+ 4·7	+ 7·1	+ 8·0	+11·6	+14·6	**+18·6**	+18·2	32·6	9·9
−16·6	−15·1	−11·2	− 2·0	+ 2·3	+ 2·0	+ 8·2	+ 6·1	+11·3	+12·9	+14·0	+17·9	**+21·5**	40·2	11·3
−22·4	−18·3	−12·2	− 5·4	+ 0·6	+ 0·8	+ 2·7	+ 6·2	+ 8·7	+18·6	+22·7	**+26·5**	+25·0	52·5	13·5
−48·4	−31·8	−22·3	−10·9	− 5·4	+ 2·2	+12·0	+17·7	+40·3	+51·5	+54·5	**+56·2**	+55·8	104·6	31·8
γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
+ 4·2	+ 3·1	**+ 4·7**	+ 4·1	+ 4·0	+ 2·2	+ 2·8	+ 4·2	+ 3·4	+ 2·6	+ 3·8	− 0·4	+ 0·3	11·3	3·3
+ 4·4	+ 2·5	+ 8·1	**+ 9·4**	+ 7·2	+ 7·3	+ 4·9	+ 4·2	+ 6·1	+ 5·7	+ 4·1	+ 2·1	− 2·1	18·6	5·5
− 1·5	+ 8·3	**+12·2**	+11·0	+ 8·8	+ 7·3	+10·5	+ 9·6	+ 6·2	+ 5·9	+ 8·4	+ 4·4	+ 0·3	24·8	7·7
+ 4·6	+10·6	+12·2	+14·1	**+18·5**	+12·9	+11·6	+11·4	+11·9	+10·9	+ 9·6	+ 5·3	− 2·7	37·7	11·1
+ 9·6	+19·4	+23·7	+24·8	+25·2	+26·7	+30·0	+29·5	**+30·2**	+21·1	+10·9	+ 9·5	−10·7	66·7	22·1
+ 3·4	+ 8·0	+ 9·0	**+10·6**	+ 9·0	+ 6·7	+ 7·0	+ 7·4	+ 8·6	+ 8·8	+ 7·1	+ 3·1	− 1·4	30·2	7·8
+ 7·9	+13·5	+13·0	**+14·4**	+13·2	+10·3	+11·0	+12·5	+11·2	+10·8	+ 9·2	+ 4·3	− 2·6	41·7	11·4
+16·3	+17·2	**+24·2**	+19·3	+13·2	+11·9	+15·2	+17·0	+13·6	+16·1	+10·8	+ 0·3	−11·5	53·0	15·2
+11·2	+12·6	+15·1	+18·9	**+27·9**	+18·5	+16·3	+15·4	+13·1	+20·7	+17·8	+ 3·8	−12·2	61·0	16·3
+33·2	+37·7	+41·2	**+45·0**	+44·5	+17·6	+19·7	+21·3	+13·4	+ 4·0	− 0·2	−12·2	−35·8	89·3	26·0
+ 4·8	+ 3·7	**+ 5·0**	+ 4·1	+ 3·9	+ 1·8	+ 2·4	+ 3·7	+ 2·3	+ 1·8	+ 2·8	− 1·5	− 0·8	10·4	3·0
+ 5·8	+ 3·7	+ 8·6	**+ 9·6**	+ 6·7	+ 6·5	+ 4·4	+ 3·4	+ 5·2	+ 4·4	+ 2·5	+ 0·1	− 4·0	19·8	5·2
+ 0·3	+ 9·8	**+13·3**	+11·1	+ 8·5	+ 7·0	+ 9·6	+ 8·9	+ 5·0	+ 4·5	+ 6·9	+ 2·5	− 2·0	24·9	7·2
+ 6·9	+12·5	+13·4	+14·6	**+18·3**	+12·7	+11·2	+10·7	+10·9	+ 8·9	+ 7·1	+ 2·4	− 5·3	35·8	10·8
+14·7	+22·6	+25·9	+25·8	+25·6	+26·3	**+28·5**	+27·4	+25·7	+15·5	+ 5·0	+ 3·5	−16·5	64·1	21·3
− 4·7	− 5·0	− 2·5	+ 0·2	+ 1·4	+ 3·5	+ 3·4	+ 4·1	+ 9·4	+ 6·6	+ 8·5	+ 9·6	+ 9·5	21·3	6·2
−11·2	− 9·8	− 3·3	− 0·9	+ 4·6	+ 6·8	+ 4·8	+ 6·9	+ 7·9	+11·1	+13·6	**+16·9**	+16·1	30·5	9·0
−15·0	−12·6	− 8·6	− 0·5	+ 3·1	+ 2·7	+ 8·6	+ 6·6	+10·8	+12·3	+13·5	+16·6	**+19·3**	36·7	10·5
−19·5	−15·2	− 9·5	− 3·2	+ 2·7	+ 2·2	+ 3·8	+ 6·9	+ 9·2	+18·0	+21·5	**+24·4**	+22·1	48·0	12·5
−42·2	−26·2	−17·2	− 6·8	− 1·9	+ 5·1	+14·3	+19·3	+39·7	+48·6	+50·1	**+51·5**	+48·7	94·3	29·2

Table VI.—Adelie Land Diurnal Inequalities.

Element.	Mean Character of class.	1 h.	2 h.	3 h.	4 h.	5 h.	6 h.	7 h.	8 h.	9 h.	10 h.	11 h.
		′	′	′	′	′	′	′	′	′	′	′
D	0·04	+25·4	+16·8	+ 1·3	− 7·9	−14·6	−18·6	−18·5	−13·9	−13·5	−13·8	−12·5
	0·15	+20·1	+15·0	+10·4	− 7·5	−15·1	−24·0	−16·4	−15·2	−15·7	−17·6	−17·3
	0·33	+30·2	+19·1	+ 6·6	− 9·9	−20·7	−26·9	−27·9	−26·4	−26·5	−23·5	−23·0
	0·64	+23·3	+22·8	+ 6·3	− 2·7	−20·5	−31·8	−36·7	−36·3	−40·0	−46·4	−43·0
	1·20	+34·7	+43·0	+32·2	+19·4	− 5·8	−40·7	−61·3	−66·9	−81·1	−64·8	−78·6
		γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
H	0·04	+ 1·8	− 4·1	− 0·6	− 8·4	− 4·8	− 7·5	− 9·7	− 6·0	− 7·6	− 6·2	− 2·4
	0·15	− 0·4	− 2·8	−21·3	−16·2	−15·0	−13·7	− 8·1	− 5·4	− 5·7	− 6·6	− 1·9
	0·33	− 7·8	−16·5	−10·7	−19·4	−28·9	−21·9	−12·7	− 5·2	− 3·5	− 1·2	+ 1·0
	0·64	− 4·3	− 9·8	−18·2	−33·7	−20·4	−21·4	−21·9	−13·3	− 8·1	− 5·5	+ 3·0
	1·20	− 8·7	−14·8	−27·0	−53·9	−65·9	−59·8	−63·0	−50·4	−41·6	− 9·6	+14·3
V	0·04	− 6·0	−17·0	−31·7	−29·1	−25·5	−16·2	− 2·4	+ 1·5	+ 2·6	+ 2·9	+ 6·8
	0·15	−17·9	−38·1	−51·7	−37·0	−34·8	−27·9	− 5·1	− 0·8	+ 3·3	+ 5·1	+11·4
	0·33	−15·5	−28·5	−40·7	−44·1	−43·0	−25·9	−10·3	− 6·3	− 0·3	+ 1·0	+ 7·0
	0·64	−18·2	−35·1	−50·9	−40·7	−33·4	−25·3	−11·5	− 7·7	+ 3·2	+ 7·7	+22·6
	1·18	−28·7	−43·9	−57·9	−65·7	−60·3	−38·0	−24·7	− 9·8	+15·0	+24·1	+34·3
N	0·04	− 0·7	− 5·6	− 1·1	− 7·3	− 3·1	− 5·4	− 7·6	− 4·4	− 6·0	− 4·6	− 0·9
	0·15	− 2·5	− 4·4	−22·2	−15·3	−13·3	−11·1	− 6·3	− 3·8	− 4·0	− 4·7	− 0·1
	0·33	−11·0	−18·4	−11·3	−18·2	−24·5	−18·9	− 9·6	− 2·4	− 0·7	+ 1·3	+ 3·4
	0·64	− 6·6	−12·2	−18·7	−33·2	−18·1	−17·9	−17·9	− 9·4	− 3·8	− 0·5	+ 7·5
	1·20	−12·3	−19·3	−30·2	−55·6	−64·8	−55·1	−56·1	−43·0	−32·7	− 2·7	+22·5
W	0·04	+23·0	+14·6	+ 1·1	− 8·0	−13·6	−17·5	−17·7	−13·2	−13·0	−13·1	−11·5
	0·15	+18·0	+13·1	+ 6·8	− 8·6	−15·3	−23·1	−15·6	−14·3	−14·7	−16·6	−15·7
	0·33	+26·1	+15·2	+ 4·6	−11·2	−21·7	−26·7	−26·5	−24·3	−24·2	−21·2	−20·5
	0·64	+19·5	+19·3	+ 3·5	− 6·4	−20·8	−31·0	−35·5	−34·1	−36·8	−42·2	−38·2
	1·20	+30·1	+36·8	+25·7	+11·0	−13·0	−43·5	−62·4	−65·9	−77·6	−59·2	−68·7

At Eskdalemuir the inclusion or omission of the vertical force range in the criterion appears of minor moment, but 1912 was a quiet year, and in a highly disturbed year it might be otherwise. At the lower end of the international scale both sets of Eskdalemuir figures suggest rather a lack of delicacy of the criterion, especially in summer. At both Antarctic stations the value of the criterion rises rapidly and fairly steadily as the international figure rises from 0·0 to 0·5. The figures for the higher classes depended on a smaller number of days, and are naturally somewhat irregular, but the general tendency to increase with the international figure is conspicuous. The omission of ΔV^2 makes a large difference to the absolute value of the criterion at the Antarctic stations, especially Adelie Land. The omission could evidently not be justified on the ground that the quantity neglected was trifling. If the criterion were used for the intercomparison of stations, the omission of ΔV^2 would tend to reduce the difference between stations in low and high latitudes.

At Eskdalemuir the significance of the international figure in 1912 varied comparatively little with the season. But in the Antarctic stations any one of the lower international figures answers to much larger movements in equinox than in winter.

§ 12. We have considered here only a few of the more outstanding magnetic

Equinox, 1912. G.M.T.

12 h.	13 h.	14 h.	15 h.	16 h.	17 h.	18 h.	19 h.	20 h.	21 h.	22 h.	23 h.	24 h.	Range	A.D.
′	′	′	′	′	′	′	′	′	′	′	′	′	′	′
−14·7	− 8·6	− 5·5	+ 1·6	+ 2·6	+ 0·2	+ 4·1	+ 4·1	+ 4·8	+ 9·9	+16·4	+23·9	+30·8	49·4	11·8
−21·7	−19·3	−13·3	− 2·2	− 0·5	+ 1·1	+10·0	+10·6	+11·3	+14·9	+25·5	+34·5	+32·5	58·5	15·5
−25·1	−12·9	− 9·7	+ 1·1	+ 4·3	+ 7·9	+ 7·9	+10·4	+19·8	+30·0	+32·5	+29·4	+33·5	61·4	19·4
−35·3	−15·9	− 6·3	+ 1·6	+ 8·1	+10·9	+16·4	+22·4	+33·1	+40·0	+47·2	+42·9	+40·5	93·6	26·2
−66·2	−37·5	−11·9	− 0·6	+12·5	+27·2	+37·6	+31·6	+43·1	+66·1	+61·1	+50·1	+57·3	147·2	43·0
γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ
− 0·1	+ 7·0	+ 7·6	+ 7·0	+ 3·4	+ 5·5	+ 3·3	+ 4·7	+ 4·1	+ 6·8	+ 4·7	+ 3·0	− 1·8	17·3	4·9
+ 3·2	+ 8·6	+12·1	+12·5	+10·6	+11·7	+12·2	+11·4	+ 8·0	+10·1	+ 2·9	− 1·5	− 4·8	33·8	8·6
+ 0·6	+ 9·9	+ 8·6	+ 9·5	+ 9·8	+10·5	+ 9·8	+10·8	+13·8	+13·1	+13·4	+ 8·7	+ 6·5	40·7	10·5
+ 9·6	+13·1	+11·2	+13·5	+12·8	+13·3	+12·7	+17·7	+15·3	+18·3	+ 6·9	+ 6·0	+ 3·5	52·0	13·1
+15·8	+26·4	+29·8	+39·1	+40·2	+39·4	+42·4	+36·6	+31·4	+25·3	+21·4	+15·9	+17·0	108·3	32·9
+ 8·6	+11·9	+11·9	+ 6·7	+ 7·4	+ 9·3	+ 8·6	+ 6·0	+ 9·0	+12·6	+11·0	+ 8·8	+ 2·2	44·3	10·6
+15·4	+20·3	+22·8	+14·8	+14·1	+14·8	+15·5	+16·1	+20·2	+22·2	+19·3	+ 8·5	−10·4	74·5	18·6
+13·1	+15·1	+18·5	+13·6	+14·3	+15·0	+16·4	+23·1	+23·1	+24·8	+15·5	+12·7	+ 1·7	68·9	17·9
+26·1	+20·9	+17·9	+13·5	+15·1	+16·6	+18·3	+27·7	+19·1	+18·4	+ 8·8	− 6·6	− 6·0	78·6	19·6
+41·4	+35·8	+26·2	+20·3	+19·8	+18·1	+17·8	+33·7	+19·9	+14·2	+20·5	+ 2·6	−14·7	107·1	28·6
+ 1·5	+ 7·9	+ 8·1	+ 6·8	+ 3·0	+ 5·4	+ 2·8	+ 4·1	+ 3·5	+ 5·6	+ 2·8	+ 0·2	− 5·1	15·7	4·3
+ 5·5	+10·6	+13·4	+12·6	+10·6	+11·5	+11·1	+11·2	+ 6·7	+ 8·4	+ 0·2	− 5·1	− 8·2	35·6	8·5
+ 3·3	+11·2	+ 9·6	+ 9·3	+ 9·3	+ 9·6	+ 8·9	+ 9·6	+11·6	+ 9·8	+ 9·9	+ 5·5	+ 2·9	36·1	9·6
+13·3	+14·7	+11·8	+13·2	+11·9	+12·0	+10·9	+15·2	+11·7	+13·9	+ 1·9	+ 1·4	− 0·8	48·4	11·6
+22·7	+30·2	+30·9	+38·9	+38·6	+36·2	+38·1	+33·0	+26·6	+18·1	+14·8	+10·5	+10·8	103·7	31·0
−13·2	− 6·9	− 4·1	+ 2·4	+ 2·7	+ 0·8	+ 4·0	+ 4·2	+ 4·8	+ 9·6	+15·2	+21·7	+27·4	45·1	11·0
−19·1	−16·3	−10·5	− 0·5	+ 0·8	+ 2·4	+10·4	+10·8	+11·1	+14·5	+23·2	+30·7	+28·5	53·8	14·2
−22·4	−10·4	− 7·7	+ 2·1	+ 5·0	+ 8·3	+ 8·2	+10·6	+19·4	+28·4	+30·7	+27·4	+30·8	57·5	18·1
−30·5	−12·7	− 4·3	+ 3·0	+ 8·8	+11·3	+16·2	+22·2	+31·5	+38·0	+43·1	+39·2	+36·7	85·3	24·4
−57·5	−30·5	− 7·1	+ 4·1	+15·9	+29·0	+38·7	+32·6	+42·3	+62·2	+57·3	+46·8	+53·3	139·8	40·5

phenomena in high magnetic latitudes, with the hope that they will suffice to show the great wealth of opportunities which magnetic observations in these latitudes provide. The sensitiveness of Antarctic (and presumably Arctic) diurnal inequalities to disturbance provides, as it were, a delicate pulse for the finger of the magnetician. What is the merest flutter in temperate latitudes is a well-marked pulsation in the Antarctic.

As it so happens, the years for which we have Antarctic magnetic records, 1902-3 and 1911-13, all fell near sunspot minimum. In one way this may have been fortunate, as it may prove that the amplitude of magnetic changes near sunspot maximum renders their registration difficult. Still, with suitably insensitive magnetographs, even the largest conceivable movements could be registered, and it is to be hoped that before many years have passed data will be obtained from the Antarctic at sunspot maximum.

Another great desideratum is a comparison of synchronous records from the Arctic and Antarctic.

Table VII.—International "Character" Figures and Disturbance Criterion Ratios.

Date.	May.				June.				July.				August.			
	I.	Esk.	C.E.	A.L.	I.	Esk.	C.E.	A.L.	I.	Esk.	C.E.	A.L.	I.	Esk.	C.E.	A.L.
1	0·1	0·6	0·2	0·2	1·0	1·2	1·5	4·5	0·3	1·1		0·8	0·9	1·1	4·3	1·3
2	0·5	0·7	1·0	0·5	0·8	1·0	2·4	0·9	0·2	0·7		0·1	0·3	0·5	0·5	1·2
3	0·6	0·9		0·8	0·8	1·1	1·8	0·9	0·9	1·9	0·9	0·7	0·2	0·3	0·5	0·7
4	0·5	0·6		0·8	0·2	0·8	0·2	0·3	1·3	3·3	4·9	2·6	0·0	0·5	0·1	0·1
5	1·3	3·5	7·4		0·0	0·7	0·1	0·3	1·2	2·0	6·9	3·8	0·9	1·2		0·7
6	0·9	0·9	1·0	3·2	0·1	0·6		0·1	0·7	0·7	1·7	9·4	1·7	7·6		3·3
7	0·8	1·7	1·0	1·7	0·6	0·7	0·2	0·1	0·6	1·0	0·7	0·4	0·5	0·5	0·5	0·5
8	0·7	0·6	0·8	0·5	1·2	2·7	5·8	5·9	0·5	1·0	1·4	1·4	0·0	0·4	0·2	0·1
9	0·1	0·4	0·1	0·4	0·9	1·8	3·7	5·1	0·1	0·7	0·4	0·5	0·0	0·3	0·2	0·3
10	0·2	0·4	0·4	0·4	0·9	1·7	2·2	1·9	0·1	0·6	0·1	0·1	0·3	0·6	0·3	0·4
11	0·6	0·8	0·2	5·2	0·6	0·8	0·8	1·2	0·0	0·4	0·2		0·2	0·4	0·2	0·2
12	1·3	2·7	4·3	5·8	0·3	0·8	0·6	0·4	0·0	0·6	0·1		0·0	0·5	0·0	0·1
13	1·4	5·6	6·5	2·2	0·1	0·8	0·2	0·2	0·1	0·6	0·0		0·0	0·5	0·1	0·1
14	1·0	1·2	2·4	1·5	0·2	0·7	0·5	0·6	0·6	1·2	0·1	0·1	0·5	0·8	0·4	0·3
15	0·3	0·4	0·6	0·5	0·1	0·8		0·1	0·0	0·8	0·2	0·1	0·4	0·4	0·2	0·2
16	0·1	0·5	0·2	1·1	0·1	1·0		0·1	0·5	0·7	0·9	0·5	0·4	0·9	0·6	0·5
17	0·2	0·4	0·3	0·3	0·3	1·0	0·1	0·1	0·5	1·1	1·0	0·5	0·9	1·2	3·2	2·5
18	0·2	0·7	0·1	0·6	0·2	0·9	0·1	0·3	0·2	0·8	0·3	0·2	1·0	1·6	2·1	3·2
19	0·4	0·7	0·4	0·5	0·1	0·5	0·1	0·1	0·1	1·0	0·3	0·1	0·9	1·4	2·9	1·3
20	0·3	0·7	0·2	0·4	0·1	0·4	0·0	0·1	0·7	1·0	1·3	0·6	0·2	0·4	0·4	0·6
21	0·2	0·6	0·2	0·2	0·2	0·7	0·1	0·1	0·4	1·0	0·8	0·6	0·6	0·7	1·3	1·3
22	0·1	0·6	0·1	0·1	0·6	0·7	0·2	0·2	0·1	0·6	0·3	0·2	1·1	2·0	3·0	2·6
23	0·1	0·4	0·0	0·1	0·9	1·0	0·4	0·6	0·1	0·7	0·4	0·2	0·9	1·2	2·1	4·3
24	0·3	0·5	0·1	0·2	0·6	1·0	0·5	0·5	0·0	0·6	0·1	0·1	0·4	0·7	1·2	0·7
25	0·1	0·4	0·1	0·2	0·2	0·7	0·2		0·3	1·0	0·4	0·4	0·3	0·5	0·9	0·6
26	0·1	0·6	0·2	0·1	0·2	0·5	0·2	0·2	0·7	0·8	1·0	0·9	0·1	0·6	0·4	0·4
27	0·2	0·6	0·1	0·1	0·8	1·9	2·3		0·8	0·9	1·5	0·8	0·8	1·3	1·1	1·0
28	0·0	0·5	0·2	0·6	0·9	1·1	1·1		0·1	0·4	0·2	0·1	0·7	0·7	0·8	0·6
29	0·8	1·2	0·2	0·5	0·8	1·5	1·2		0·0	0·5	0·3	0·2	0·4	0·5	0·6	0·9
30	0·6	0·8	0·3	0·4	0·3	0·6	0·4		0·3	0·5	0·7	0·5	0·3		0·4	0·4
31	0·8	1·1	0·5	0·4					1·1	2·9	2·0	2·1	0·3	0·5	0·5	0·5
Criterion (Unit $100\,\gamma^2$).		96	547	594		80	462	843		73	246	381		121	501	950

Table VIII.—International "Character" Figures and Disturbance Criterion Ratios.

Date.	April.				September.				October.			
	I.	Esk.	C.E.	A.L.	I.	Esk.	C.E.	A.L.	I.	Esk.	C.E.	A.L.
1	0·1	0·5	0·2		0·3	0·5	0·5	0·8	1·0	2·1	2·3	3·0
2	0·3	0·7	0·2		0·1	0·3	0·2	0·2	0·0		0·3	0·3
3	0·4	0·7	0·7	0·9	0·6	0·8	0·2	0·3	0·6	0·5	0·7	0·7
4	0·3	0·5	0·4		0·7	0·9	1·1	1·6	0·3	0·5		0·6
5	1·3	3·7	2·8		0·5	0·6	1·0	1·0	0·0	0·5	0·3	0·3
6	1·0	3·5	2·0		0·4	0·4	0·8	0·7	0·1	0·6	0·2	0·4
7	0·8	1·6	1·6	1·0	0·1	0·3	0·3	0·4	0·4	0·7	0·7	0·4
8	0·1	0·5	0·2		0·6	0·6	0·7	0·7	0·3	0·6	1·0	0·9
9	0·1	0·7	0·4	0·4	0·7	0·7	0·8	1·2	0·2	0·3	0·6	0·7
10	1·0	1·3	2·4		0·2	0·3	0·5	0·8	0·4			0·9
11	0·1	0·3	0·3	0·2	0·4	0·3	0·5	0·8	1·2		1·1	1·4
12	0·2	0·5	0·3	0·5	0·6	0·5	1·6	1·0	0·8		1·6	1·3
13	0·2	0·4	0·5	0·6	0·3	0·4	1·0	1·0	0·9	1·2	1·4	1·1
14	0·8	1·0	0·4	0·4	0·3	0·3	0·6	0·5	1·6	10·4	5·0	3·4
15	1·3	2·5	3·2	3·1	0·0	0·4	0·1	0·2	1·3	3·4	2·7	2·6
16	1·0	1·8	4·6	2·3	0·0	0·3	0·4	0·5	0·9	1·4	1·5	1·1
17	1·0	1·2	2·7	1·9	1·8	10·2	3·4	2·1	0·7	0·8	0·9	1·1
18	0·6	1·0	1·8	1·2	1·1	1·0	2·8	2·6	0·0	0·2	0·3	0·4
19	0·6	0·9	0·9	0·6	0·4	0·4	1·2	0·9	0·0	0·3	0·3	0·3
20	0·5	0·8	1·4	1·1	0·5	0·7	1·0	0·9	0·7	0·4	0·9	1·5
21	0·0	0·6	0·2	0·2	0·1	0·3	0·7	1·1	0·3	0·4	0·5	1·2
22	0·1	0·6	0·6		0·7	0·9	1·0	1·8	0·4	0·3	0·8	0·9
23	0·3	0·7	0·4	0·3	0·9	0·7	0·8	1·2	0·3	0·4	0·7	0·9
24	0·2	0·3	0·6		1·6	5·4	6·3	4·5	0·2	0·4	0·5	0·3
25	0·3	0·5	0·5		0·3	0·5	0·4	0·8	0·3	0·3	0·6	0·8
26	0·1	0·3	0·1		0·6		0·6	0·7	0·0	0·3	0·5	0·4
27	0·2	0·5	0·2		0·0	0·4	0·3	0·3	0·3	0·4	1·0	0·7
28	0·1	0·7	0·1		0·0	0·4	0·2	0·3	0·7	0·4	1·0	1·6
29	0·1	0·7	0·1		0·2	1·1	0·4	0·2	0·1	0·2	0·4	0·9
30	0·3	0·7	0·2	0·3	0·3	0·4	0·5	1·0	0·2	0·2	0·7	0·5
31									0·1	0·1	0·7	0·6
Criterion (Unit 100 γ^2).		90	577	1285		137	495	886		90	630	1257

Table IX.—International "Character" Figures and Disturbance Criterion Ratios.

May to August.

Month.	Place.	Quiet Days.	International Characters. 0·1 to 0·2.	International Characters. 0·3 to 0·4.	International Characters. 0·5 to 0·8.	Distd. Days.
May.	I.	0·10	0·17	0·32	0·66	1·18
	Esk.	0·54	0·50	0·58	0·93	2·78
	C.E.	0·14	0·19	0·32	0·57	4·32
	A.L.	0·24	0·43	0·67	0·99	4·40
June	I.	0·08	0·18	0·30	0·70	0·98
	Esk.	0·60	0·76	0·80	1·09	1·70
	C.E.	0·07	0·21	0·37	1·18	2·86
	A.L.	0·14	0·26	0·25	0·63	4·35
July	I.	0·02	0·12	0·32	0·62	1·06
	Esk.	0·60	0·69	0·90	0·93	2·20
	C.E.	0·14	0·27	0·63	1·07	3·24
	A.L.	0·10	0·20	0·57	1·62	2·00
August.	I.	0·02	0·20	0·34	0·62	1·12
	Esk.	0·50	0·37	0·57	0·80	2·76
	C.E.	0·16	0·37	0·58	0·82	2·67
	A.L.	0·16	0·50	0·60	0·74	2·22
Mean.	I.	0·06	0·17	0·32	0·65	1·08
	Esk.	0·56	0·58	0·71	0·94	2·36
	C.E.	0·13	0·26	0·48	0·91	3·27
	A.L.	0·16	0·35	0·52	0·99	3·24

Equinoctial Months.

Month.	Place.	Quiet Days.	International Characters. 0·1 to 0·2.	International Characters. 0·3 to 0·4.	International Characters. 0·5 to 0·8.	Distd. Days.
April	I.	0·08	0·15	0·32	0·66	1·12
	Esk.	0·52	0·50	0·63	1·06	2·56
	C.E.	0·20	0·35	0·40	1·22	3·00
	A.L.	0·20	0·50	0·50	0·86	2·70
Sept.	I.	0·02	0·15	0·34	0·60	1·22
	Esk.	0·36	0·50	0·40	0·69	3·64
	C.E.	0·24	0·48	0·69	0·86	2·88
	A.L.	0·30	0·62	0·81	0·95	2·40
October	I.	0·02	0·16	0·33	0·70	1·20
	Esk.	0·28	0·34	0·45	0·53	4·28
	C.E.	0·38	0·48	0·76	1·02	2·50
	A.L.	0·38	0·56	0·81	1·24	2·30
Mean.	I.	0·04	0·15	0·33	0·65	1·18
	Esk.	0·39	0·45	0·49	0·76	3·49
	C.E.	0·27	0·44	0·62	1·03	2·79
	A.L.	0·29	0·56	0·71	1·02	2·47

Table X.—International "Character" Figures and absolute values of Disturbance Criterion (Unit $100\gamma^2$).

Criterion.	Station.	Season.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0 and 1·1	1·2 and larger.
$\Delta N^2+\Delta W^2+\Delta V^2$	Eskdalemuir	May, June, August	53	51	53	61	77	70	74	70	123	128	161 (1·02)	453 (1·38)
		Equinox	41	44	48	51	51	82	79	81	119	108	171 (1·02)	651 (1·48)
$\Delta N'^2+\Delta W'^2+\Delta V'^2$	Cape Evans	May to August	58	76	119	210	290	323	220	408	604	1051	1031 (1·04)	2758 (1·28)
		Equinox	168	183	283	321	426	595	506	536	716	732	1588 (1·02)	1977 (1·44)
$\Delta D^2+(H\Delta D)^2+\Delta V^2$	Adelie Land	May to August	136	159	292	465	478	589	458	1447	810	1838	2325 (1·04)	3449 (1·35)
		Equinox	351	571	616	859	870	1037	789	1558	1102	1264	2865 (1·02)	3827 (1·40)
$\Delta N^2+\Delta W^2$	Eskdalemuir	May to August	46	47	51	58	72	66	71	63	111	116	157 (1·04)	326 (1·34)
		Equinox	38	41	45	47	46	76	75	75	112	90	152 (1·02)	596 (1·48)
$\Delta N'^2+\Delta W'^2$	Cape Evans	May to August	50	64	105	180	263	278	188	343	480	887	863 (1·04)	2153 (1·28)
		Equinox	136	145	237	265	353	540	430	455	620	647	1221 (1·02)	1750 (1·44)
$\Delta H^2+(H\Delta D)^2$	Adelie Land	May to August	58	79	138	236	279	287	260	987	440	1069	1227 (1·04)	1839 (1·35)
		Equinox	210	244	355	472	510	647	571	953	692	850	1726 (1·03)	1964 (1·47)

Investigation on X-Rays and β-Rays by the Cloud Method. Part II.—β-Rays.

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(Received June 23, 1923.)

[Plates 16–24.]

The greater part of the material used in the study of the β-ray tracks was obtained during the experiments with X-rays described in Part I. A number of photographs were also taken of the tracks of fast β-particles emitted by radio-active substances or ejected from the walls of the cloud chamber by γ-rays. Some photographs of α-ray tracks were obtained during the course of these experiments; these have been published elsewhere.*

1. *General Character of β-ray Tracks.*

The tracks of the fastest β-ray particles in air are generally perfectly straight over distances of many centimetres. Within the last 10 cms. of its range the deviations in the path of a β-ray are very marked and become more and more so as the velocity of the particle diminishes. Fig. 1 (Plate 16) shows in a striking way the contrast between the paths of fast and slow β-particles.

The deviations are of three types :—

(1) A gradual bending due to an accumulation of small deviations; (2) a sudden deviation due to a close encounter with an electron which is in consequence ejected with sufficient velocity to form a branch track; and (3) a sudden bend due to the passage of a β-particle close to the nucleus of an atom; this is generally unaccompanied by any branch track and the deviation is generally through a large angle, not infrequently approaching 180°. Figs. 2, 3, 10, 11, 12 illustrate the different kinds of deviation in the last few centimetres of the path.

The increase in the ionisation as the velocity of the β-particle diminishes is well shown by the increasing density of the cloud track as the end of range is approached.

2. *Range and Velocity.*

I have not thus far attempted to make accurate measurements of the ranges of β-particles of known velocity. The measurements, already described in

* 'Proc. Camb. Phil. Soc.,' vol. 31, p. 405 (1923).

Part I, Section 4, of the ranges of β-particles due to characteristic radiations from metals show that from ranges between $0 \cdot 2$ mm. and $1 \cdot 5$ cm. Whiddington's law* holds approximately; and the range is proportional to the square of the kinetic energy. To give a range of 1 cm. the energy of the β-particle has to be the equivalent of about 21,000 volts. The range is measured along the track in the three-dimensional picture and reduced to normal pressure. The comparative ranges of the β-particles due to the K-radiations of copper and silver are shown in figs. 4 and 5.

The fourth-power law connecting range and velocity is in accordance with Sir J. J. Thomson's theory† of ionisation by β-particles. The range of a β-particle of given initial velocity depends on the rate at which it loses energy along its path as a result of collisions. Some variation in the ranges of β-particles of given length are therefore to be expected; for example, a particle may meet with more than the average number of collisions in which a large amount of energy is transferred to ejected electrons, and may thus have an abnormally short range. An extreme case is that of a β-ray track with a visible branch; such a track is in general of considerably less than the average range. It was found, however, that the initial kinetic energy of a β-particle which produced a branched track could generally be obtained with considerable accuracy from measurements made on the track. To do this the energies of the primary and secondary β-particles immediately after the encounter were deduced from their ranges; the two branches could then be replaced by a single track of range corresponding to the sum of these energies. The equivalent range of the whole track as thus completed was generally found to be in quite good agreement with that of the unbranched tracks when approximately homogeneous radiation was used.

3. *Ionisation along the Path of a β-ray.*

Among the photographs of β-ray tracks obtained in 1912‡ were some in which the cloud tracks were resolved into droplets, and in which, in addition to single pairs of ions, groups containing several pairs appeared along the track. The occurrence of these groups was taken as indicating that in many cases an electron is ejected from an atom by the action of the β-particles with sufficient velocity to produce other ions by collision—secondary ionisation. This interpretation has been confirmed by the more recent work; the largest groups are

* 'Roy. Soc. Proc.,' A, vol. 86, p. 360 (1912).

† 'Phil. Mag.,' vol. 23, p. 449 (1912).

‡ 'Roy. Soc. Proc.,' A, vol. 87, p. 277.

indistinguishable from very short branch tracks. The number and distribution of the ions along the path of a β-particle have been found to be in general accordance with the theory introduced by Sir J. J. Thomson* and developed by Bohr† and others.

Depending upon the conditions of the experiment (pressure, expansion, ratio, timing of the various events and magnitude of the electric field) different degrees of sharpness or diffuseness of the cloud tracks formed by condensation on the ions may result. It is assumed that the illumination and focussing are sufficiently good to give a sharp image of any isolated cloud particle; these are generally small enough to act virtually as point sources of light. The diffuseness of the tracks then depends on the extent to which the ions have been dispersed by the action of the electric field and by diffusion and mutual repulsion before being fixed by condensation of water.

There are three cases which are specially suitable for studying different aspects of the problem of the ionisation along the path of the β-particle.

To determine the number of groups per cm. of the tracks—*i.e.*, the primary ionisation, or number of atoms from which the original β-particle ejects an electron—each track must be sufficiently sharp to prevent confusion of successive groups (fig. 7, Plate 19).

To obtain the total ionisation, primary and secondary, the ions must be separated sufficiently to ensure that each gives an easily resolvable cloud particle; the electric field must be strong enough to ensure separation of the positive and negative ions of each pair. The conditions may be made such that the positive and negative ions form separate diffuse tracks, as happens when the β-particle passes through the gas before the expansion (fig. 9); but separation of the positive and negative tracks is not essential (fig. 8).

The most interesting case is the intermediate one, in which not only are the individual groups readily distinguished, but each group is resolvable into its component drops; so that both the number and distribution of the ions produced by the β-particle are obtained. In this case both the number of electrons ejected from atoms of the gas by the primary β-particle (along a limited portion of its path) and the number of ions produced by each electron thus ejected are recorded in the photograph (fig. 6).

Results.—The primary ionisation—given by the number of groups per cm. along the β-ray track—is more easily measured than the total ionisation per

* J. J. Thomson, *loc. cit.*

† N. Bohr, 'Phil. Mag.,' vol. 30, p. 581 (1915); S. Rosseland, 'Phil. Mag.,' vol. 45, p. 65 (1923).

centimetre ; this is fortunate, as it is with the primary ionisation that theories of ionisation along the path of a β-particle more directly deal.

Most of the measurements have been made on the initial portions of the tracks of β-rays excited in air by X-rays. Counts were made of the groups per cm. in 46 such tracks and included considerably more than 1,000 groups.

The tracks were all formed in air at pressures below 20 cms. of mercury, and the groups (including single pairs) in the initial one or two cms. of the tracks were counted. The number per cm. at atmospheric pressure was deduced on the assumption that the ionisation is proportional to the pressure.

These measurements gave for the primary ionisation (number of groups per cm.) a mean of 96 per cm. at a distance of about 1·5 cm. from the end of the β-ray track in air at atmospheric pressure. Numbers equal to 104 groups per cm. and 83 groups per cm. were obtained for the primary ionisation at about 1 cm. and 2 cms. from the end of the range respectively ; but only a small number of observations were available for these portions of the range.

The velocity of the β-particle at 1·5 cm. from the end of its range was deduced from measurements of the range of β-particles of known velocity. (See Part I, Section 4.)

The velocity of the β-particles at 1·5 cm. from the end of its range is found in this way to be $9{\cdot}5 \times 10^9$ cms. per sec., corresponding to about 25,000 volts ; it is for a velocity of approximately this magnitude that the value of 96 per cm. found for the primary ionisation by the β-particle applies. According to Thomson's theory the ionisation per cm. should vary inversely as the square of the velocity of the β-particle ; the values found for the ionisations at 1, 1·5 and 2 cms. from the end of the range are in approximate agreement with this relation. The velocity $9{\cdot}5 \times 10^9$ differs so little from 10^{10} cms. per second that we may safely deduce the primary ionisation at the latter velocity, on the assumption that the ionisation varies inversely as the square of the velocity.

The primary ionisation due to a β-particle having a velocity of 10^{10} cms. per second is about 90 per cm. in air at 760 mm. and 20° C. ; *i.e.* it ejects an electron from about 90 atoms per cm. of its path.

Sir J. J. Thomson obtained the expression $\mathrm{I} = \dfrac{2\pi \mathrm{N} n e^4}{m_0 u^2 \mathrm{W}}$ for the primary ionisation per cm. along the path of a β-ray, N being the number of molecules per c.c., n the number of effective electrons per molecule, m_0 the mass of the electron, e the electronic charge, u the velocity of the β-particle, and W the

work required to remove an electron from the molecule; it is assumed that m_0u^2 is large in comparison with W. If we make use of the results now obtained for the primary ionisation in air ($I = 96$, when $u = 9{\cdot}5 \times 10^9$) and put $n = 10$ the number of electrons, other than those of the K-level, in the nitrogen molecule, we obtain for W the value $6{\cdot}8e/300$; *i.e.*, to remove an electron from the molecule the potential required is 6·8 volts. This is less than half the ionising potential as given by recent work, and is very near the "resonance" potential, 7·5 volts. There may be an error of 10 per cent. in the determination of u^2 and therefore of W; experimental error cannot account for the large difference between W and the ionisation potential.

The tracks of nine fast β-particles from Radium and Thorium and their products, and one from an unknown source (it appeared in a picture of the tracks of β-particles due to X-rays), were also found to be suitable for direct determination of the primary ionisation. All these tracks were almost perfectly straight. The air pressure varied between 18 and 50 mm. of mercury.

The primary ionisation in the paths of these fast β particles amounted in all cases, when reduced to atmospheric pressure, to between 18 and 22, the mean being 20 per cm. If we assume the primary ionisation to vary inversely as the square of the velocity (in accordance with Thomson's theory and with W. Wilson's measurements in the ionisation by very fast β-rays) we deduce from the primary ionisation as the mean velocity of these fast β-particles, $2{\cdot}1 \times 10^{10}$ cm. per second.

It would obviously be of interest to have direct determinations of the primary ionisation due to fast β-rays of known velocity. The only method available for determining the velocity of the particles which produced the tracks used in the above measurements of the primary ionisation depended on the existence of branch tracks. Several tracks of fast β-particles had such branches, and in one case at least the conditions admitted of a fairly definite measurement. From the range of the branch track the velocity of the ejected electron was obtained, while the angle through which the β-particle was deflected by the encounter gave a measure of the ratio of the momenta of the ejected electron and the deflected β-particle.

While no great accuracy could be claimed for the measurement it was sufficient to show that the velocity of the β-particle exceeded 2×10^{10} cms. per sec. The primary ionisation found for this track was 23 per cm.

These observations on fast β-rays point to the conclusion that the primary ionisation continues to vary approximately as the inverse square of the

velocity of the β-particle up to velocities as great as two-thirds of that of light.

As already mentioned, a few photographs have been obtained in which not only is the cloud track, which has been formed by the passage of a β-particle. resolvable into its component groups (each indicating the expulsion of an electron from an atom by the original β-ray) but each group is resolved into its component droplets. Each droplet represents a single ion.

Eight β-rays produced by X-rays have furnished tracks of which considerable portions showed this double resolution. The total number of groups in the resolved portions of these tracks was 128. Of these 55 consisted of single pairs of ions, there were 29 groups of four ions, 16 of six, 13 of eight, and 16 groups of more than eight ions.

One of the fast β-ray tracks which was resolved into groups—one described above as from an unknown source—also had its groups themselves resolved into drops (fig. 6). Out of 24 groups there were 13 pairs, 5 fours, 2 sixes, 2 eights, 1 ten and one unresolved larger group.

The fact that the single pair is the commonest kind of group, and that the frequency of occurrence continually diminishes as the number of ions in the group increases, is in accordance with the Thomson-Bohr theory.

The measurement of the total ionisation (primary + secondary) per cm. of a β-ray track is subject to the following difficulty. Comparatively large groups of ions (set free by electrons which have been ejected with considerable velocity) occur at intervals along the track, and the ionisation found per cm. is very different according as the portion of the track in which we make the count is made to include such a group or to stop short of it. The total ionisation per cm. of a β-ray track is in a sense essentially indeterminate and the above practical difficulty is merely an illustration of this fact. In an extreme case the ejected electron or secondary β-particle may have such a velocity that it forms a well defined branch to the primary track; in this case it would plainly be absurd to include the total ionisation produced by the secondary β-ray in the ionisation per unit length of the primary β-ray track. And the matter is not essentially different when the secondary β-ray has too small a velocity to form a recognisable branch track. The total ionisation due to a β-ray (as distinct from the ionisation per cm.) is free from this ambiguity, since the ionisation produced by all its secondary β-rays, including visible branches, is obviously to be included.

The ratio of the whole ionisation per cm. to the primary ionisation, obtained by dividing half the total number of drops in the above double resolvable

tracks by the number of resolved groups amounts to 1·9. For the fast β-ray track the ratio is 1·8. We undoubtedly get in this way too low a value for the mean ratio of total ionisation per cm. to primary ionisation per cm., because only smaller groups are included, these being the only ones which can be resolved.

The ionisation per cm. (primary + secondary) was also determined in the case of six diffuse tracks of range about 1·5 cm., in which the groups were too diffuse to be separated from one another. The mean number of pairs of ions per cm. (at atmospheric pressure) was 337, *i.e.*, 3·5 times the value found, in the same region of the β-ray track, for the primary ionisation; but the number per cm. of the different tracks varied between 272 and 416. This large variation is not surprising in view of the difficulty to which reference was made above. To illustrate this difficulty it may be mentioned that one resolved group on the track of a fast β-ray, which was divided into completely separated positive and negative components, showed about 75 droplets in the positive and an equal number in the negative cloud.

While the value found for the whole ionisation per cm. is much more uncertain than that found for the primary ionisation alone, it may be taken as between 3 and 4 times the primary when the range of the β-particle is about 1·5 cm., *i.e.*, when its velocity is about 10^{10} cms. per sec.

It is of interest to calculate the energy given, according to Thomson's theory, by the β-particle to electrons ejected from the atoms per cm. of its path; and to compare this, on the one hand, with the total energy lost per cm. (known from the relation between ranges and voltages), and, on the other, with the energy equivalent of the secondary ionisations due to the ejected electrons.

The number of cases per cm. of the path of a β-particle in which it gives to an electron energy exceeding a given value W is

$$\mathrm{I} = \frac{\pi e^4 \mathrm{N} n}{\mathrm{T}}\left(\frac{1}{\mathrm{W}} - \frac{1}{\mathrm{T}}\right) \text{ where } \mathrm{T} = \tfrac{1}{2} m_0 u^2.$$

Thus

$$\frac{d\mathrm{I}}{d\mathrm{W}} = -\frac{\pi e^4 \mathrm{N} n}{\mathrm{T}\mathrm{W}^2}.$$

The energy transferred per cm. of its path by the β-particle to the electrons is

$$-\frac{d\mathrm{E}}{dx} = \int \mathrm{W}\,d\mathrm{I} = \frac{\pi e^4 \mathrm{N} n}{\mathrm{T}} \int \frac{d\mathrm{W}}{\mathrm{W}}$$

$$= \frac{\pi e^4 \mathrm{N} n}{\mathrm{T}} \log_e \frac{\mathrm{W}_2}{\mathrm{W}_1},$$

where W_1 is the energy required to get an electron out of the atom, and W_2 may be taken to be the energy which an ejected electron must acquire to produce a just recognisable branch track. (The arbitrariness of the upper limit of W corresponds exactly to the practical difficulty in the measurement of the total ionisation per cm. to which reference was made above.) It is assumed that the velocity of the β-particle is small enough to allow the change of effective mass with velocity to be ignored.

If there are two classes of electrons in the molecule (*e.g.*, outer electrons and K-electrons) requiring different energies W_1 W_k to eject them, then

$$-\frac{dE}{dx} = \frac{\pi e^4 N}{T}\left(n_1 \log\frac{W_2}{W_1} + n_2 \log\frac{W_2}{W_k}\right).$$

The energy W_2 required to enable an ejected electron to produce a visible branch is in the neighbourhood of 1,500 volts; while W_1 is about 10 volts. The ratio W_2/W_1 is about 150; even if we take W_2/W_1 as 200 instead of 150 we only alter log W_2/W_1 by about 5 per cent. It is thus unnecessary to know with accuracy the limits W_2 W_1.

If we insert the known values of the constants in the above equation we have for the case of nitrogen (which will give very nearly the same result as air), at 760 cm. and 20° C., the loss of energy of the β-particle in volts,

$$-\frac{dV}{dx} = \frac{9 \times 10^7}{V} \text{ volts per cm.}$$

This is the calculated loss of voltage by the β-particle per cm. due to energy transferred to the ejected electrons. The actual total loss of volts per cm. is known from the experimentally determined relation between the range and kinetic energy of the β-particle, expressed in volts,

$$V = 21000\,R^{\frac{1}{2}}$$

and is equal to $\dfrac{2 \cdot 2 \times 10^8}{V}$ volts.

Rather less than half the total loss of energy of the β-particle is accounted for by the energy which, according to Thomson's theory, is given to the ejected electrons.

The ionisation when V is about 25,000 volts is (according to the rather scanty data available) about 340 pairs per cm.; of the 340 negative ions about 95 represent the electrons ejected by the primary β-ray. The calculated energy given to these electrons by the primary β-particle is $9 \times 10^7/(2 \cdot 5 \times 10^4) = 3 \cdot 5 \times 10^3$ volts, *i.e.*, $3 \cdot 5 \times 10^3/95 = 37$ volts per electron ejected by the primary β-particle, or about $3 \cdot 5 \times 10^3/340 = 10$ volts per pair of ions (primary

and secondary) produced. The total energy actually lost per cm. by a β-particle when its energy corresponds to about 25,000 volts is approximately $2 \cdot 2 \times 10^8/2 \cdot 5 \times 10^4 =$ about $8 \cdot 8 \times 10^3$ volts, *i.e.*, about $8 \cdot 8 \times 10^3/95 = 93$ volts per electron ejected, or $8 \cdot 8 \times 10^3/340 = 26$ volts per pair of ions produced.

A part of the energy of the primary β-particle which is not used in ejecting electrons is spent in exciting radiation in the atoms traversed; electrons which derive from the primary β-particle too little energy to enable them to escape from the atom may acquire enough to raise them above the radiation energy level.

We may calculate the number of collisions per cm. in which the transfer of energy from the β-particle to an electron lies between the resonance and ionisation limits, and hence obtain also an estimate of the energy lost in this way per cm. of its path by the β-particle. The calculated energy loss in radiation collisions of this kind amounts, however, to less than 1/10 of the magnitude found above for the energy lost by the β-particle otherwise than in ejecting electrons.

To obtain a sufficient total loss of energy by non-ionising collisions we have to suppose that the β-particle may lose energy in an encounter with an atom even when the encounter is such that the energy lost is a very small fraction of the equivalent of the normal resonance potential.

The conditions along the track of a β-particle, of which the energy is very great compared with resonance or ionising potentials, are very different from those of experiments on ionising potentials, which are made with comparatively slow electrons at low pressures. It is possible that resonance radiations when once excited may be continually overtaking the β-particle and being absorbed and re-emitted along its track. Collisions which would otherwise have been ineffective (unaccompanied by any loss of energy of the β-particle) may possibly be made effective through this absorption of resonance radiation; at the same time certain collisions which would otherwise have resulted in the production of radiation only, may in the same way become ionising collisions. Again, a portion of the radiation from atoms traversed by the primary β-particle may be absorbed in atoms traversed by the ejected electrons and so assist in producing secondary ionisation.

It may be to such absorption of resonance radiations, already excited by the β-particle in previous encounters, that we have to look for an explanation of (1) the excess of the loss of energy along the path of the β-ray over the sum of the calculated losses due to ejection of electrons and excitement of resonance radiation, (2) the excess of the primary ionisation over that calculated according

to Thomson's theory, and (3) discrepancy between the small amount of energy available on that theory from the primary ejected electrons as compared with the number of ions finally produced (10 volts per pair). It is also possible that it may afford an explanation of curvature in β-ray tracks (see Sections 8 and 9).

4. *Ejection of Electrons from the K-Level.*

The number of electrons ejected from the K-level of the nitrogen in 1 cm. of air by a β-particle would according to the Thomson-Bohr theory amount to about 1/120 of those ejected from the outer levels. (It is assumed that the energy of the β-particle is large compared with that required to remove an electron from the K-level.) Thus we should expect rather less than one K-electron to be ejected per cm. of the path of a β-particle of which the range was comparable with 1·5 cms. When, however, the velocity of the β-particle only amounts to a few times that of the K-electrons in the atom (as it does in the last few tenths of a mm. of its range) the chance of ejection of an electron from the K-level is much greater.

There are two ways in which cases of the ejection of an electron from the K-level of an atom might possibly be recognised. The energy of the ejected electron after escaping from the parent atom will be less than if it came from an outer level by the energy difference of these levels; the velocity of the secondary electron as deduced from its range may be expected to be less than that deduced from the deflexion of the primary β-ray. Again the ejection of the K-electron will be followed by the emission of a quantum of K-radiation; this might be absorbed by a neighbouring atom and give rise to a short characteristic β-ray track. Such short β-ray tracks (due to absorption of K-radiations of the gas) are frequently found near the origins of the primary β-rays when these are produced in air by X-rays. They also sometimes occur in the neighbourhood of the ends of β-ray tracks. They are extremely rare near other portions of the tracks. It is possible that such characteristic radiations are much more readily absorbed in the track itself than elsewhere; in the case of such absorption the resulting secondary β-ray would not be immediately distinguishable from one ejected by the direct action of the primary β-ray alone.

5. *Branch Tracks* (Figs. 10, 11, 12, 13).

The chance of occurrence of a branch track exceeding a given length may, on Thomson's theory, be calculated if we know the energy of a β-particle of

given range. The energy of a β-particle of 1 mm. range corresponds to about 6,600 volts. (To eject an electron from the K-level of nitrogen or oxygen with velocity sufficient to produce a track of 1 mm. range would require about 400 additional volts.) From Thomson's theory we deduce, that the chance of a branch of longer range than 1 mm. occurring between 1 and 2 cms. from the end of a β-ray track in air at normal pressure is about 1 in 10.

The numbers found by actual counting, while of the right order of magnitude, are somewhat smaller than the theory would predict. In the initial 2 cms. (corresponding to 5 mm. at normal pressure) of 344 tracks in air at a pressure of 19 cms. of mercury there were 12 branches exceeding 4 mms. in length (= 1 mm. at atmospheric pressure); the range of the primary β-rays was between 1 and 2 cms. The number of branches found in this region of the range amounts to 0·07 per cm. of the primary track (at normal pressure) as compared with about 0·10 according to the theory. Again 990 tracks of average range about 1·5 cms. had 65 branches with ranges of more than 1 mm.; the count in this case being made along the whole available length of the primary track. The number of branches per primary track of about 1·5 cm. range is thus about 0·07; according to the theory it should be about twice as great. Many of the tracks were however of less than 1 cm. in range; and, again, of the longer tracks the terminal portion was frequently missing from the photograph; the discrepancy may possibly nearly all be accounted for in this way.

A count was also made of the branches which exceeded 1 mm. in length (= 0·25 mm. in range at normal pressure) in air at a pressure of 1/4 of an atmosphere; the number in the initial 2 cms. of the tracks (= 0·5 cm. at atmospheric pressure) was counted. The average range of the tracks was about 1·5 cm. at normal pressure. In 362 tracks 36 such branches were counted; *i.e.*, a mean of 0·10 branch, exceeding 0·25 mm. in range, per $\frac{1}{2}$ mm. of track of 1·5 cm. range. Substituting for the ranges of the β-particles the equivalent voltages, we may say that the mean number of electrons ejected with energy corresponding to more than 3,300 volts, by a β-particle of energy corresponding to about 25,000 volts, is 0·20 per cm. This is almost identical with the calculated number.

In the great majority of cases of branched tracks the branch is approximately perpendicular to the deviated β-ray track; this is the result to be expected when the encounter is between two equal masses, one of which is initially at rest. The atomic electrons are not at rest, and in addition they may suffer deviations during or after ejection from the atom; so that we should not

expect the angle to be exactly 90°. Except however in the case of β-rays of extremely short range the velocity of the electrons within the atom is relatively small.

Branches on the tracks of very fast β-particles from radio-active substances generally make with the deviated β-ray track an angle which is appreciably less than 90°.

There are also other cases in which the angle between the branches differs greatly from 90°. In some cases the explanation may lie in the deviation of the ejected electron by forces within the atom; but when the primary β-rays are produced by the action of X-rays there is the additional possibility that the ejection of the electron which gives the branch track may also be partly due to the action of X-radiation.

On the assumption that we are dealing with a simple encounter between the β-particle and an electron, we may determine the ratio of the velocity of the deviated β-particle to that initially given to the ejected electron, by measuring the angle through which the β-ray is deflected. We may also get an estimate of the velocity of the β-particle after the encounter, and of the electron after its escape from the atom, by measuring their ranges. It is of interest to see to what extent there is agreement between the values, found by the two methods, for the ratio of the velocity of the β-particle to that of the ejected electron. Even when the plane containing the ray before and after the deviation is nearly perpendicular to the axis of the stereoscopic camera, there is generally an uncertainty of 2° or 3° in the determination of the angle of deviation. This introduces an uncertainty of 10 or 20 per cent. into the determination of the ratio of the velocities by this method. While there may possibly also be error of 10 or 20 per cent. in the measurement of the ranges (on account of the difficulty of measuring along the tracks in three-dimensions) this only corresponds at most to a 5 per cent. error in the measurement of the velocities, if the range is taken as proportional to the fourth-power of the velocity. Measurements were made on 37 branched tracks; the primary β-rays were due to the action of X-rays on air and had initial velocities less than 10^{10} cm. per second, so that the effective mass did not differ much from that of a slow-moving β-particle. Of these 37 branched tracks 16 showed an agreement between the ratios R_1, R_2, of the velocities obtained by the deviation and range methods respectively, to within 20 per cent.; the ratios themselves varied between 1 and 3·3. The mean value of R_1/R_2 for these 16 tracks is 1·005; so that the two methods give on the whole identical results. As regards the rest of the tracks (except for two in which the ratios of the

velocities obtained by the two methods differed by less than 25 per cent.) the differences in the results obtained by the two methods are far outside the range of experimental error.

In a few instances the deflection of the β-ray exceeded the value which would correspond to the range of the branch track. An abnormally large deflection of this kind may be explained as being due to the ejected electron coming from an inner level of the atom and so losing an appreciable part of its energy in escaping; or again as being the result of the β-particle having approached near enough to the nucleus to be deflected by it.

In most of the abnormal cases, however, the deflection of the β-particle is very small in comparison with what might be expected from the range of the branch track. In 17 out of the above 37 tracks the ratio of the velocity of the β-ray to that of the ejected electron, as deduced from the deflection, exceeded twice, in 14 cases three times, in 12 cases six times the ratio as deduced from the ranges. In 10 out of these 12 cases the discrepancy was much greater, the deviation of the β-ray being less than 1/10 of what would correspond to the ratio of the velocities as deduced from the ranges.

An abnormally small deflection accompanying expulsion of a secondary β-particle, like an abnormally large one, may in some cases be due to the deflecting action of the nucleus on the primary β-particle; it is unlikely, however, that nuclear deflection will in more than a few cases happen nearly to neutralise the deflection of the β-particle due to its encounter with an electron.

The expulsion of secondary β-rays of considerable range without corresponding deflection of the primary particle would seem to prove that the energy of the ejected β-particles is not always mainly derived directly from the kinetic energy of the primary β-particle. It is possible that the additional energy of the secondary β-particle, when there is little or no deflection of the primary β-particle, is derived from X-radiation, mainly secondary radiations excited in the air by the primary X-ray beam; radiation of appropriate wave-length may be more easily absorbed in the path of a β-particle than elsewhere.

The branch tracks which are associated with abnormally small deflections of the primary β-ray have in most cases a range of 3 or 4 tenths of a millimetre, corresponding to a velocity of about 4×10^9 cm. per sec. or energy about 4,000 volts. This range is approximately the same as that of the long-range δ-rays produced in air by α-rays. Again, it does not much exceed the calculated range of a β-particle ejected by argon K-radiation (energy = 3,200 volts).

6. *Two Branches from the same Point.*

One or two examples of β-ray tracks with two branches springing from the same point have been found among the photographs. A striking case is that shown in fig. 13 (Plate 22).

The chances against two electrons being independently ejected from molecules so near one another as to be unresolved in the photographs are very great. It is much more likely that the two electrons have been simultaneously ejected from one atom. Such an occurrence is of interest in connection with theories of spectra, both of ordinary light and of X-rays.*

7. *Nuclear Deflections.*

Sudden deviations not associated with branches occur fairly frequently on the β-ray tracks; a deflection of this kind is most naturally regarded as being due to the β-particle passing near the nucleus of an atom. The deviations unlike those due to encounters with electrons (which do not normally exceed 45°) have all values up to 180°. There may or may not be a pair or small group of ions at the bend; it is only rarely that there is a large group or short branch at the bend, due to a close encounter with an electron in the same atom. Examples of nuclear deflections are shown in figs. 10, 16, 17 (Plates 21 and 24).

I have not attempted to make anything approaching a complete statistical study of the nuclear bends; *i.e.*, a determination of the frequency with which any given angle of deviation is exceeded in any given portion of the range of the normal β-particle. This would be a matter for a special research.

It is possible, however, in a stereoscopic picture of β-ray tracks to recognise with some certainty whether a sudden bend exceeds or falls short of 90°. I have made a count of the number of deflections equal to or exceeding 90° in 503 tracks; the observations were confined to the portion of the tracks lying between 5 mm. and 15 mm. from the end of the range measured along the track and reduced to atmospheric pressure. In the 503 tracks there were 44 nuclear deflections of 90° or more in this portion of the range; the limiting ranges, 15 mm. and 5 mm., correspond to energies of approximately 25,000 and 15,000 volts respectively.

Thus in air at atmospheric pressure 8·8 per cent. of the β-particles suffer sudden deflections of at least 90° in the portion of the track lying between 15 mm. and 5 mm. from the end; the energy of the β-particle falls from about 25,000 to about 15,000 volts in this section of the path.

* S. Rosseland, *loc. cit.*

According to Rutherford's theory* of nuclear deflections, the fraction of the whole number of β-particles which suffers deflections exceeding 90° in a distance dx is $\mathrm{K}dx$, where

$$\mathrm{K} = \pi \mathrm{N} \left(\frac{\mathrm{E}e}{2\mathrm{T}}\right)^2$$

and N is the number of atoms per c.c., E, e the charges of the nucleus and β-particle respectively, and T the kinetic energy of the β-particle. The variation of voltage V along the path of the β-particle is given approximately by $\mathrm{V}^2 = 21000^2\, x$, where x is measured along the track from the end of the range; so that

$$\mathrm{T}^2 = \left(\frac{\mathrm{V}e}{300}\right)^2 = \frac{e^2}{300^2} \times 21000^2 x = 4{\cdot}9 \times 10^3 e^2 x.$$

Thus the fraction of the β-particles which suffers a deflection exceeding 90° between 15 and 5 mm. from the end of the range is

$$\mathrm{F} = \int \mathrm{K}\, dx = \pi \mathrm{N} \frac{\mathrm{E}^2 e^2}{4} \int \frac{1}{\mathrm{T}^2}\, dx$$

$$= \frac{\pi \mathrm{N} \mathrm{E}^2}{4 \times 4{\cdot}9 \times 10^3} \int_{0\cdot5}^{1\cdot5} \frac{1}{x}\, dx$$

$$= \frac{\pi \mathrm{N} \mathrm{E}^2}{19{\cdot}6 \times 10^3} \log 3.$$

Now F was found from the above observations to be $8{\cdot}8 \times 10^{-2}$; N, the number of atoms in air at atmospheric pressure and 15° C., is $5{\cdot}5 \times 10^{19}$; we may use the data to deduce E, the nuclear charge

$$\mathrm{E}^2 = \frac{8{\cdot}8 \times 10^{-2} \times 19{\cdot}6 \times 10^3}{\pi \times 5{\cdot}5 \times 10^{19} \times 1{\cdot}1}$$

$$\mathrm{E} = 3{\cdot}1 \times 10^{-9} \text{ e.s.u.} = 6{\cdot}5e.$$

This is very near the theoretical nuclear charge, $7e$, of the nitrogen atom.

8. *Curvature of β-ray Tracks.*

Every case of ejection of an electron by a β-particle involves a change of momentum of the β-particle, mainly in a direction perpendicular to its path and in general therefore a deviation of the primary ray. The deviation is generally easily measurable when the secondary β-particle acquires sufficient energy to enable it to produce a visible branch track. In the great majority of cases, however, the secondary electron only acquires a small fraction of

* 'Phil. Mag.,' vol. 21, p. 668 (1911).

the energy of the primary β-particle, and the individual deviations of the β-ray are small.

To do no more than just eject an electron from an atom, energy corresponding to the ionising potential (of the order of 10 volts) must be supplied. If this has come from a β-particle of range 1·5 cm. (energy about 25,000 volts) the deflection of the β-particle, given approximately by the ratio of the velocities corresponding to the above voltages, will be about 1°. This is the smallest deviation to be expected, according to the simple theory for any case of ejection of an electron by a β-particle having the above energy, and of such ejections there are nearly 100 per cm.

In addition to this large number of small deviations due to ionising encounters with the electrons of the atom, a quite comparable number of deflections of similar amount is to be expected from nuclear collisions.

That a number of successive small deviations should sometimes happen to be all in the same direction, and give to a β-ray track the appearance of possessing a continuous curvature over a short distance, is perhaps not surprising. But the curvature sometimes continues over such remarkably long distances that it is difficult to believe that it is accidental. It is quite possible to get instrumental distortion of tracks, due to air motion and other disturbing influences, but I believe that such distortion is absent in the photographs now published. The occurrence of perfectly straight tracks—of α-rays or fast β-rays—in the pictures, close to curved β-ray tracks (fig. 1), and of β-ray tracks in which the earlier portion is straight and curvature only appears in the latter part of the track (fig. 10), is sufficient evidence that the curvature belongs to the original path of the β-ray.

A thorough statistical study of the curved tracks has not been attempted. The observations which have been made indicate that curvature is not an essential property of the β-ray track, which gradually becomes more and more evident as the end of the path is approached; but rather that in certain cases, as a result of some particular kind of encounter having occurred, succeeding encounters are affected by a "bias" which favours deflection in one direction. When the curvature appears, its magnitude corresponds to an average deviation in the favoured direction of from 1° to 3° for each ionising collision; *i.e.*, it is of the order of magnitude to be expected if the bias were sufficient to make nearly all the ionising collisions result in deviations towards one side of the path, the magnitude of the deviation due to an ionising collision remaining unaltered. Both Shimizu and Compton* have called

* A. H. Compton, 'Phil. Mag.,' vol. 41, p. 279 (1921).

attention to the curvature of the tracks in some of my earlier photographs, and both drew the conclusion that, to explain the curvature, the β-particle must itself be capable of acquiring a bias by being set in rotation. There is, however, another alternative which appears to me to be a more probable one.

Many of the atoms which the β-ray has traversed have been put in a condition to emit radiation; these radiations may be continually overtaking the β-particle and affecting the nature of its succeeding encounters with electrons of other atoms, these encounters at the same time determining the absorption of the radiation. The bias causing the curvature may thus not lie in the β-particle, but in the field of radiation in which it is moving.

9. *Effects of Secondary Radiations Overtaking the β-Particle.*

Let us suppose that Thomson's equation is used to calculate the number of occasions on which the energy transferred from the β-particle to an electron exceeds any given value. In all cases in which the calculated energy transferred falls short of that necessary to bring the electron from the orbit in which it is situated to the next stationary orbit which it can occupy, there is no transfer of energy. The deviation of the β-particle due to an encounter of a given degree of closeness with an electron will depend on whether or not this transference takes place; we may describe a collision as effective in the first case and ineffective in the second.

Any influence which converts an ineffective into an effective collision will produce a definite effect on the resulting deviation of the β-particle. In an ineffective collision we might picture the absence of any transfer of energy as being due either to the force between the β-particles and electron being zero instead of having the calculated value, or, more naturally, to the force causing no displacement of the electron relatively to the nucleus; in the latter case the force is in effect exerted by the β-particle on the relatively very large mass of the nucleus or of the atom as a whole. An ineffective collision would on the first view cause no deviation of the β-particle, on the second view twice as large a deviation as an effective collision; thus the difference in the deviations due to an effective and an ineffective collision of a given degree of closeness is the same on either view, but the sign of the difference is opposite.

Any agency which converted what would otherwise have been ineffective collisions into effective ones, only when these collisions were such as to cause deviation of the β-particle in one direction but not in the opposite, would give a bias or curvature to the path of the β-particle. Radiation from an

atom which has already been traversed by the β-particle may be such an agency.

We may perhaps illustrate the essential features of the matter by considering a model of the atom in which the electrons are supposed to be initially at rest, each at its normal energy level. A β-particle may make a large number of ineffective collisions, but before it has travelled more than a small fraction of a millimetre it is likely to pass sufficiently near to an electron to displace it to the resonance energy level, or to a higher, let us say, the nth level. Let us suppose that the displaced electron immediately falls back to its normal level and that the energy radiated is all absorbed by an electron with which the β-particle is now making what would otherwise have been an ineffective collision; a collision, for example, which would not have given to the electron energy sufficient to bring it from the normal level to the resonance level, but which would have been able to bring it from the nth to the $(n+1)$th level. The original displacement of the first electron by the encounter will be perpendicular to the path of the β-particle; let it be in the y direction. The displacement of the second electron due to the falling in of the first will tend to be in the direction y. It is only when the collision tends to displace the second electron in the y direction, as distinct from the $-y$ direction, that the radiation will tend to convert an ineffective into an effective collision.

The second electron may at once in turn fall back, with emission of radiation, which again overtakes the β-particle and affects the nature of a subsequent collision. We may thus picture the radiation as being handed on from atom to atom along the path of the β-particle, and converting collisions, which would otherwise have been ineffective, into effective collisions, in such a way as to give a bias to the β-ray. Eventually the radiation would take part in the ejection of an electron and so cease to be handed on along the path of the β-particle.

It is possible that not only resonance radiation but characteristic X-radiations may be transmitted along the path of the β-particle in the above manner. We might explain in this way some of the results of Section 5, *e.g.*, the occurrence of branch tracks with abnormally small deviation of the β-ray. Quite an appreciable proportion of the β-particles ejected by the primary X-rays are likely to originate in argon atoms; the argon K-radiation thus excited may possibly be transmitted from one argon atom to another along the path of the β-particle until it is finally absorbed with ejection of an electron from some other atom through which the β-particle passes. The branch tracks accompanied by abnormally small deviations of the β-particle were, as pointed

out in Section 5, mainly of ranges only slightly exceeding that corresponding to argon K-radiation.

10. *Some Less Frequent Occurrences.*

An isolated sphere track sometimes occurs in the immediate neighbourhood of the end of a β-ray. These sphere tracks are in all probability due to characteristic radiations from an atom, from the K-level of which the primary β-ray has ejected an electron. The chance of such ejection is particularly great near the end of the range of the primary β-particle, when its energy does not greatly exceed that required to eject a K-electron ; and again there is the possibility, suggested in Section 9, that the K-radiation may have originally been excited further back in the path of the β-particle, and been handed on from atom to atom till it escapes at the end.

When a β-ray ends in or near the path of the primary beam of X-rays, the occurrence of an associated short-range track within the primary beam is apparently a much more frequent phenomenon (fig. 16) ; a long track may also sometimes have its origin in a similar position, *i.e.*, within the primary X-ray beam and close to the end of another track. These effects are in accordance with the results of Part I, Section 8 ; the secondary β-ray is apparently due to a combined action of primary and secondary X-rays.

The almost complete absence of isolated sphere tracks or scattered ions in the spaces between the long β-ray tracks, outside the primary X-ray beam, is very striking. Collisions resulting in the ejection of K-electrons cannot be very rare along the paths of the β-particles (Section 4) ; it is possible that the resulting K-radiation, as suggested in Section 4, is generally absorbed by an atom lying in the track of the primary β-ray. A few cases of sphere or other tracks have, however, been observed to originate outside the track of a primary β-particle, but very near a sudden bend in its path.

There is one very remarkable case of this kind in which a secondary β-ray track of considerable range (about 8 mm.) starts close to a sudden bend, of nearly 90°, in the track of a primary β-ray. The expansion during the series of experiments to which this belongs was completed during the passage of the X-ray discharge (Part I, Section 9). The diffuse character of the primary β-ray track, and the sharpness of that of the secondary ray, show that there was a considerable interval—of the order of 1/1000 of a second—between the ejection of the primary and secondary β-particles.

A few cases have been encountered in which the track of a β-particle is "broken," in the sense that it appears to come to a sudden end, to continue

its course again with diminished velocity (as shown by the increased ionising effect) along a laterally displaced nearly parallel line; the direction of motion may or may not be reversed (figs. 14 and 15). The appearance of these broken tracks suggests the production of a polarised X-radiation by sudden stopping of a β-ray (as a result of a nuclear collision), and the absorption of this radiation with ejection of an electron in a direction nearly parallel to the path of the primary β-particle.

A remarkable event is shown in fig. 17, where two long-range β-particles, which undoubtedly form a pair (Part I, Section 8), have been emitted upwards and downwards respectively from atoms exposed to a narrow beam of X-rays. The lower β-particle has suffered a nuclear collision, with complete reversal of its direction, and has approached very closely to the track of the other particle; the two tracks have the appearance of being twisted around one another, as if one particle were in effect attracted by the other or by its tracks. This remarkable occurrence may be a mere accident; it is however not inconceivable that secondary radiations from atoms traversed by one β-particle may so influence the nature of the encounters made by a second β-particle, which passes almost simultaneously in the immediate neighbourhood, as to cause an apparent attraction between the particles.

Summary of Results.

The tracks of fast β-particles are very nearly straight over distances of several cms. In the last few cms. of the range the deviations are large and are of three kinds: (*a*) sudden deviations often through large angles up to 180°, the result of a close approach to the nucleus of an atom; (*b*) sudden deviations ranging up to 45°, due to a close approach to an electron which is in consequence ejected to form a branch track, generally approximately at right angles to the deflected primary track; (*c*) gradual deviations due to an accumulation of deviations of *a* or *b* type, individually too small to be detected.

The range of the β-ray as measured along the track is approximately proportional to the square of the kinetic energy, or to the 4th power of the velocity (Whiddington's law), for ranges from about 0·1 cm. to 1·5 cms.; the range is 1 cm. when the kinetic energy of the particle is the equivalent of about 21,000 volts.

The primary ionisation (*i.e.*, number of atoms from which electrons are ejected by the direct action of primary β-ray) is about 90 per cm. for a velocity of 10^{10} cm. per sec. and is approximately inversely as the square of the velocity.

The total ionisation per cm., including that due to secondary β-particles of range too short to form visible branch tracks, is about 3 or 4 times as large as the primary. The primary ionisation is in agreement with Thomson's theory, if the minimum energy which the β-particle has to give to the electron to eject it is about 7 volts—approximately the resonance potential (not the ionisation potential) of nitrogen.

In portions of some of the tracks not only is the primary ionisation (number of atoms from which the β-particle has ejected an electron) recorded, but the ions which each of these electrons has itself produced are made visible and may be counted.

The number of tracks which have branches exceeding a given range, *i.e.*, which eject electrons with kinetic energy exceeding a given value, is in general agreement with Thomson's theory.

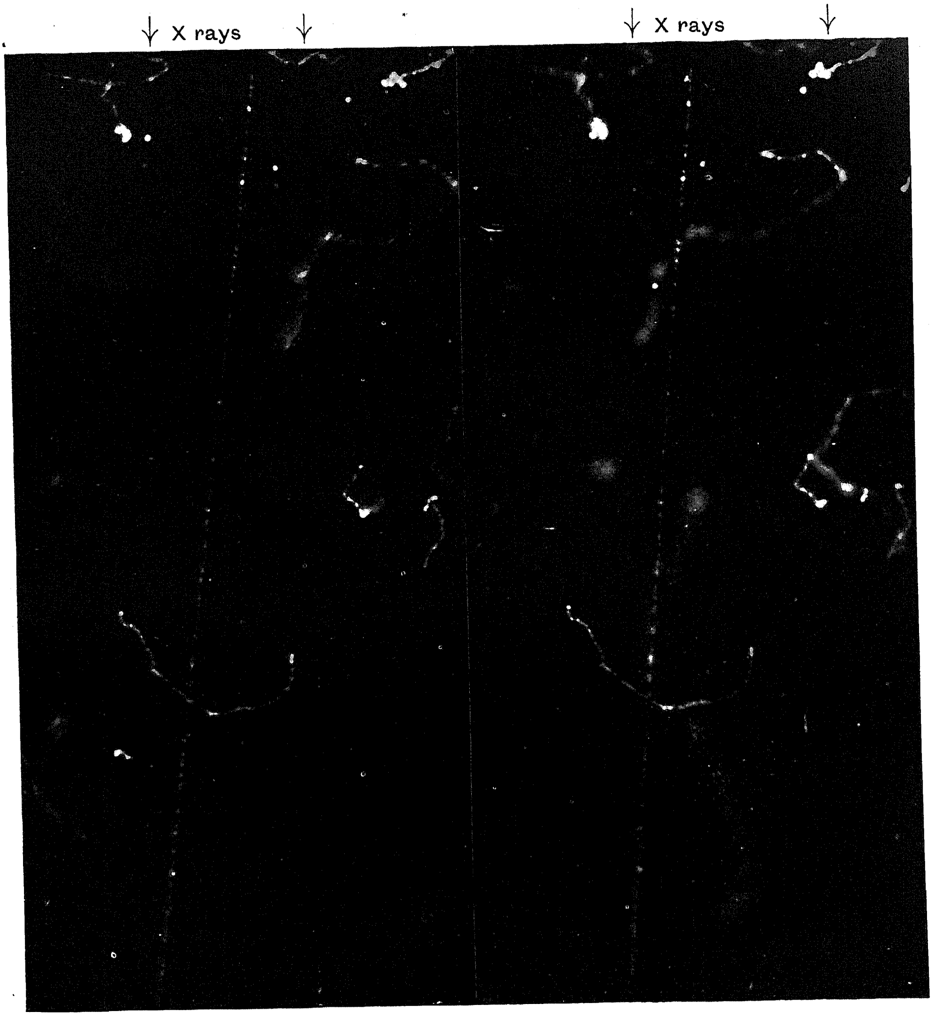
The number of tracks with nuclear deflections exceeding 1 right angle is in good agreement with Rutherford's theory and gives for the charge of the deflecting nucleus the value $6 \cdot 5\ e$, almost identical with the theoretical $7e$ of nitrogen.

In many cases of branching the ratio of the velocities as given by the ranges of the two branches is in agreement with the ratio obtained from the angles; but there are other cases in which a branch track of considerable range occurs accompanied by only a very small deviation of the primary ray.

It is suggested that many features of the β-ray tracks, including the curvature which sometimes appears, may be due to radiations which are excited in atoms by the passage of the β-particle; the radiations continually overtaking the β-particle and affecting the nature of its collisions with electrons in atoms subsequently traversed.

The work of which an account is given in this and the previous paper was carried out at the Solar Physics Observatory. I have to thank the Director, Prof. Newall, for providing me with all facilities for carrying on the work. I owe much to discussions I have had with him and with Mr. Milne. I am indebted to Mr. Stanley for the help he has given in the design of apparatus, and for constructing it in the Observatory workshop, and to Mr. Manning for making enlargements of many hundred stereoscopic pictures, a few of which are reproduced.

Fig. 1 (X 4).



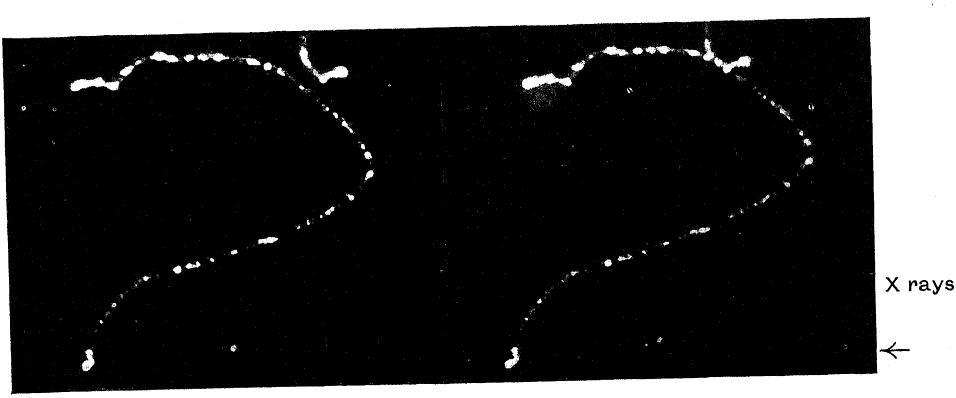
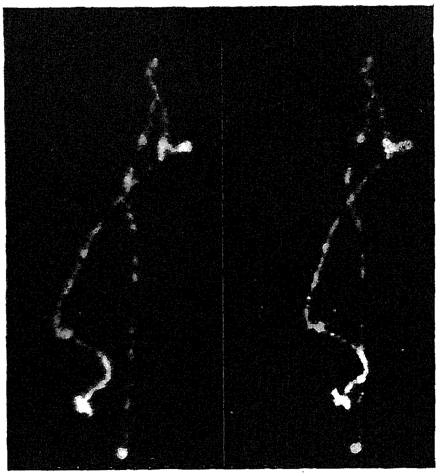


Fig. 2 (X 4).

Fig. 1. Fast and slow β ray tracks. Final pressure 55 cms.
„ 2. Final air pressure 20 cms.

Fig. 3 (X 8).



X rays

X rays X rays

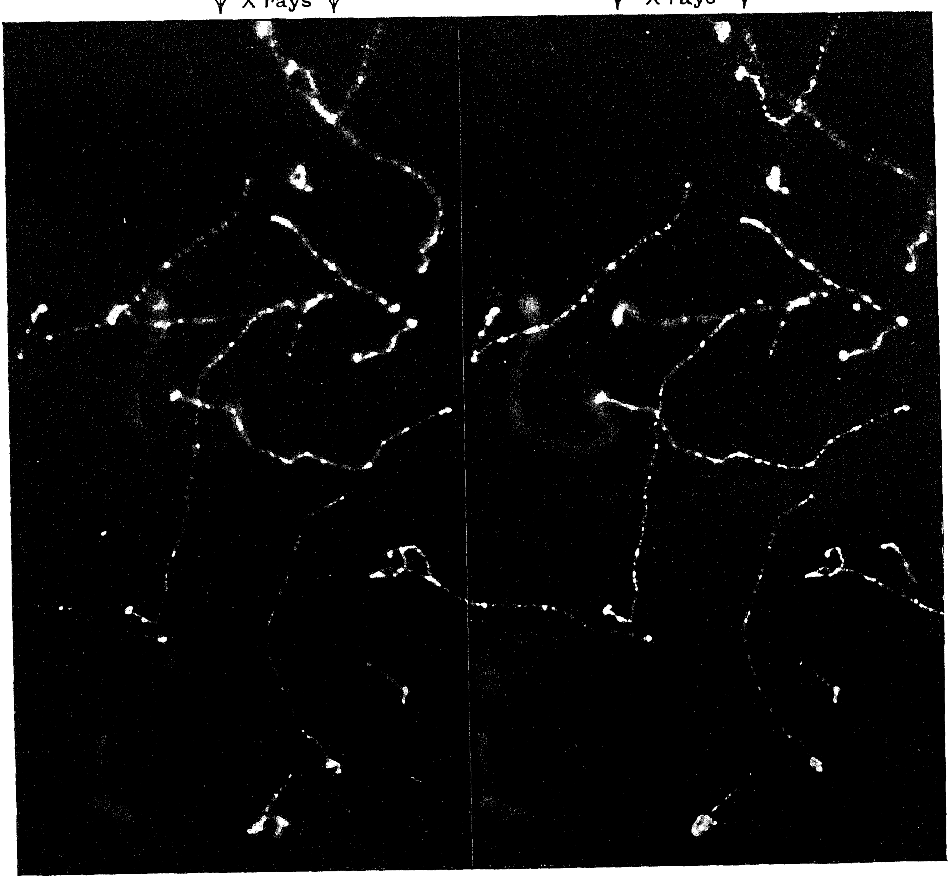
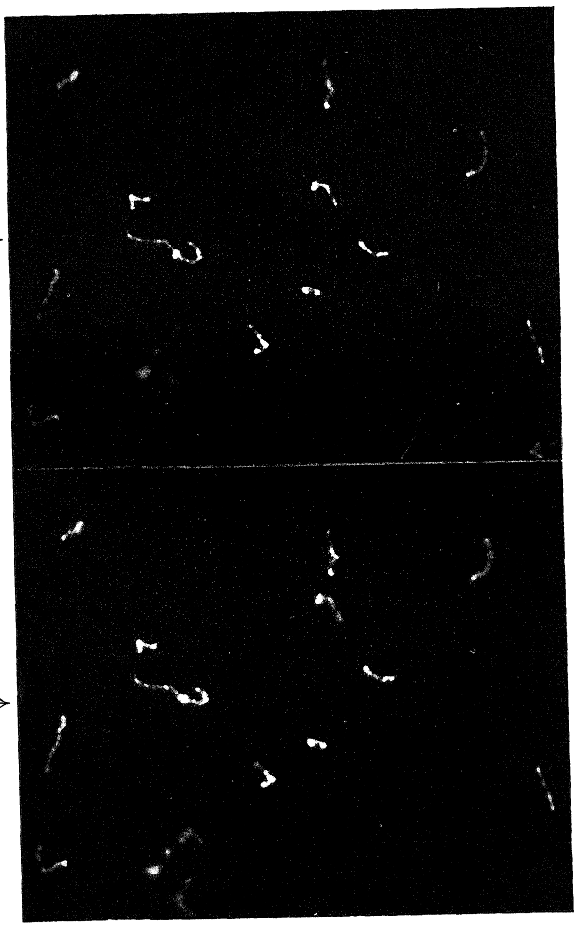


Fig. 4 (X 4).

Fig. 3. Final pressure 50 cms.
Fig. 4. β rays due to Silver K radiations. Final pressure 53 cms.

Fig. 5 (X 4).



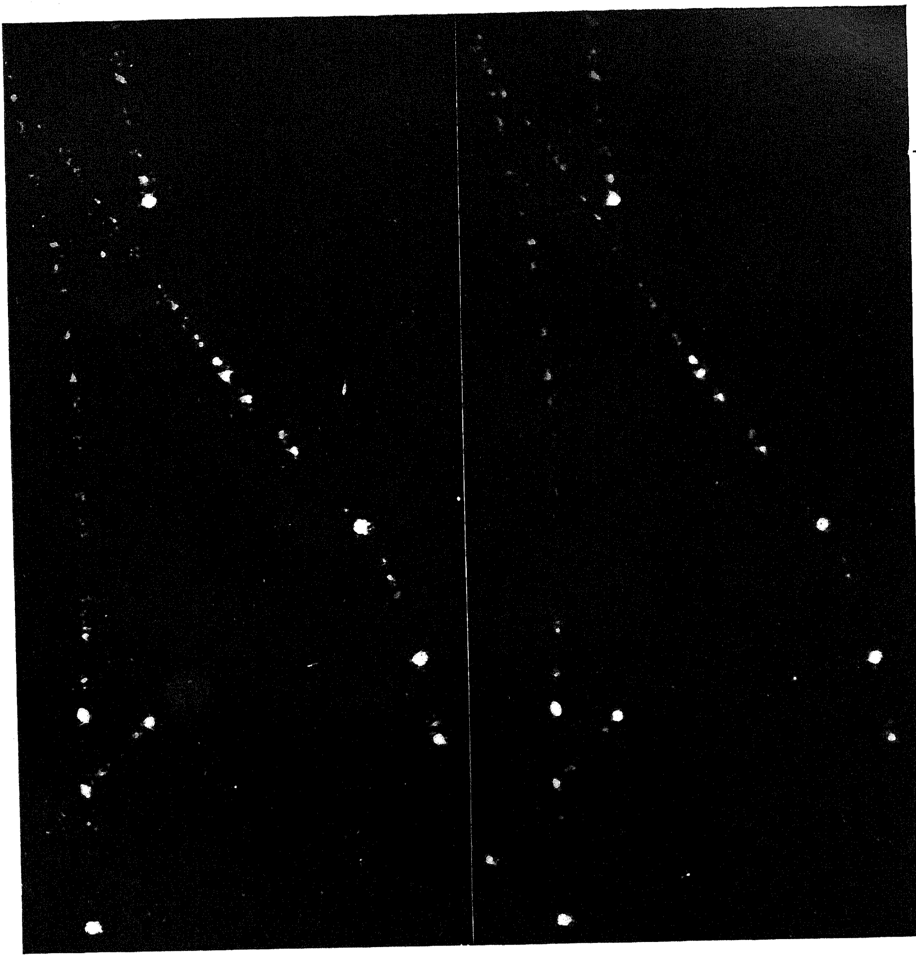
β rays due to copper K radiations.

Final pressure 53 cms.

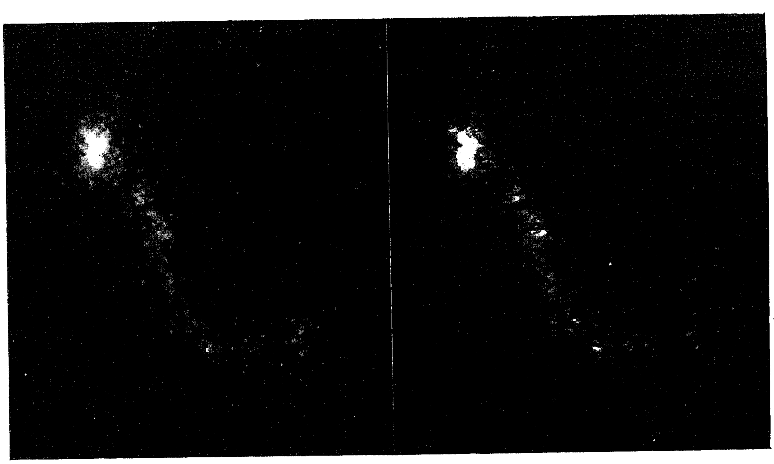
Fig. 6 (X 8).

Track of fast β ray showing groups resolved. Final pressure 20 cms.

Fig. 7 (X 8).



X rays



X rays

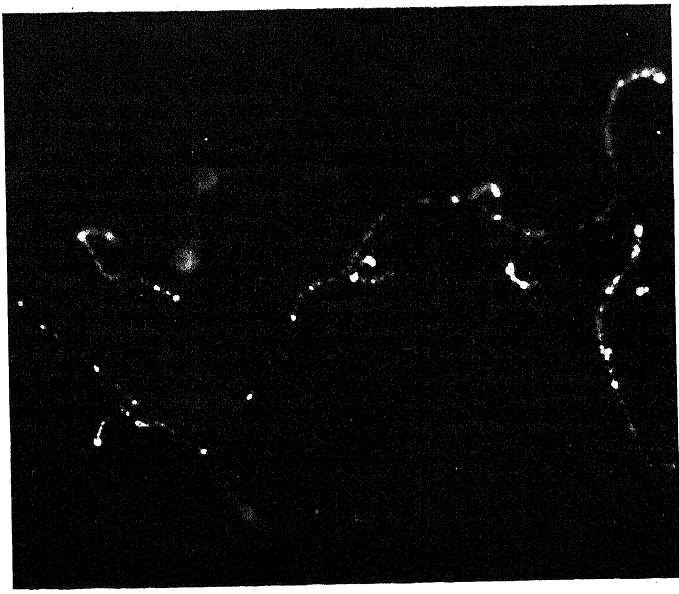
Fig. 8 (X 8).

Resolved tracks (Section 3). Fig. 7. Final pressure 18 mm.
Fig. 8. Final pressure 11 cms. "Fish track" (Part 1, Section 7).

Fig. 9 ($\times 2\frac{1}{4}$).

Tracks divided into positive (upper) and negative (lower) components. The X rays passed before the expansion and the positive and negative ions travelled upwards and downwards respectively under the action of the vertical electric field before being fixed by condensation of water. Final pressure 50 cms.

Fig. 10 (X 4).



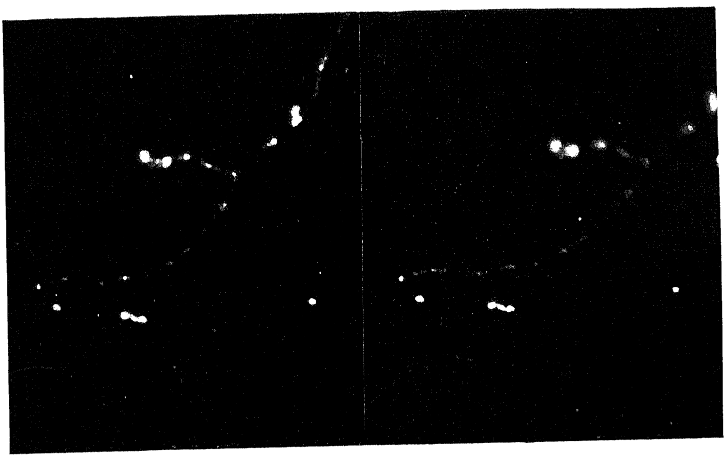
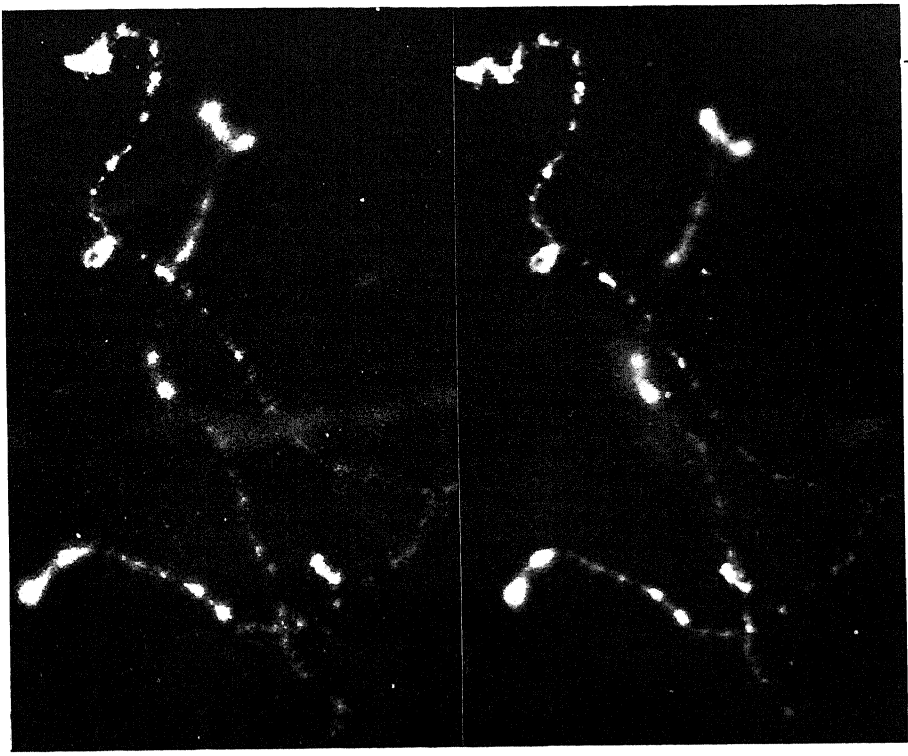


Fig. 11 (X 4).

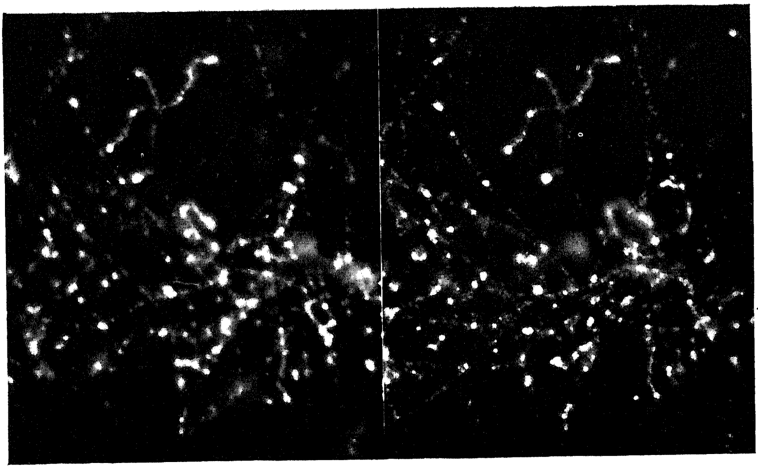
Fig. 10. Track starts with large backward component (Part I, Section 6). Initial straight portion, nuclear bend, branches; curvature in later portion of track. Final pressure 20 cms.

Fig. 11. Branched track. Final pressure 20 cms. Near origin of main track is associated "sphere" track (Part I, Section 8).

Fig. 12 (X 8).



X rays

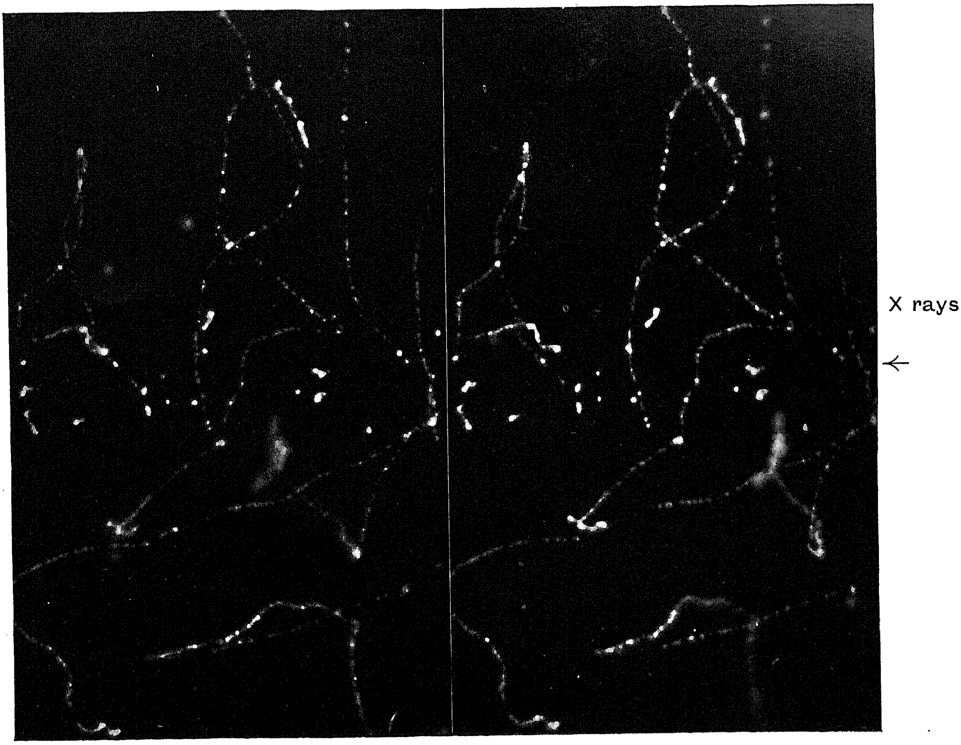


X rays

Fig. 13 (X 4).

Fig. 12. Branched track. Final pressure 18 cms.
" 13. Two simultaneous branches (Section 6). Final pressure 18 cms.

Fig. 14 (X 4).



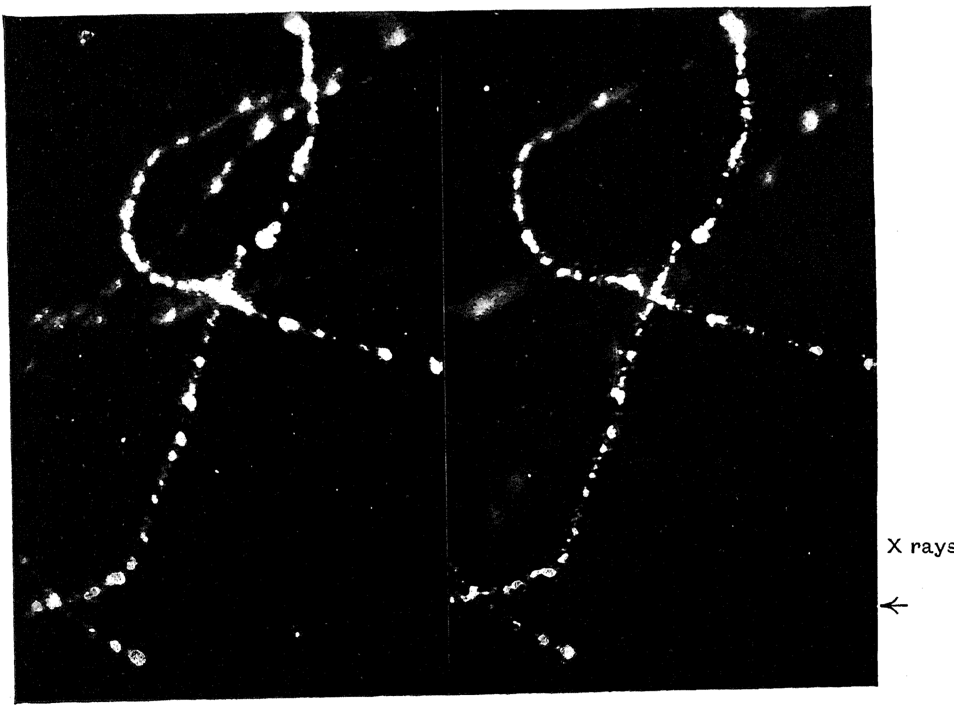
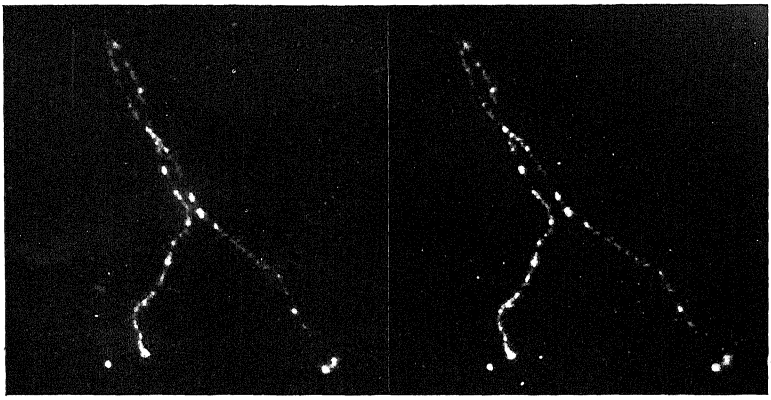


Fig. 15 (X 8).

Broken tracks. (Section 10.) Fig. 14. Final pressure 50 cms.
Fig. 15. Final pressure 19 cms.

Fig. 16 (X 8).



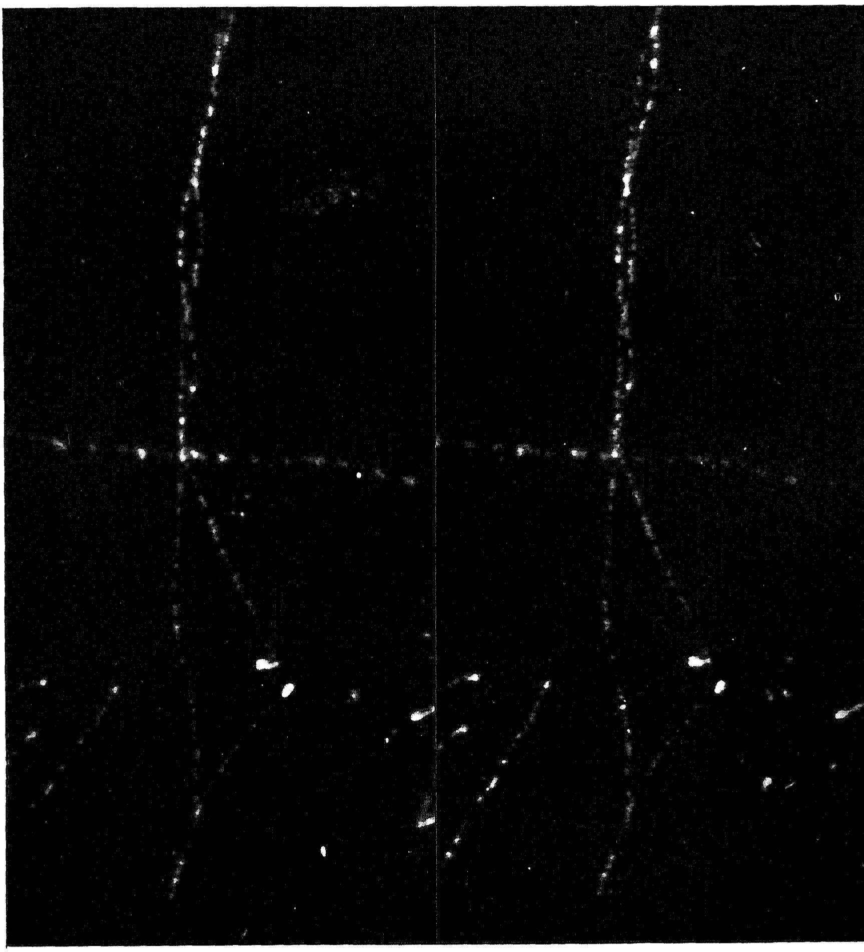


Fig. 17 (X 8).

(Section 10.) Fig. 16. Final Pressure 19 cms.
,, 17. Final pressure 55 cms.

Experiments on the Motion of Solid Bodies in Rotating Fluids.

By G. I. Taylor, F.R.S.

(Received July 17, 1923.)

[Plate 25.]

Some years ago it was pointed out by Prof. Proudman* that all slow steady motions of a rotating liquid must be two-dimensional. If the motion is produced by moving a cylindrical object slowly through the liquid in such a way that its axis remains parallel to the axis of rotation, or if a two-dimensional motion is conceived as already existing, it seems clear that it will remain two-dimensional. If a slow three-dimensional motion is produced, then it cannot be a steady one. On the other hand, if an attempt is made to produce a slow steady motion by moving a three-dimensional body† with a small uniform velocity (relative to axes which rotate with the fluid) three possibilities present themselves :—

(*a*) The motion in the liquid may never become steady, however long the body goes on moving.

(*b*) The motion may be steady but it may not be small in the neighbourhood of the body.

(*c*) The motion may be steady and two-dimensional.

In considering these three possibilities it seems very unlikely that (*a*) will be the true one. In an infinite rotating fluid the disturbance produced by starting the motion of the body might go on spreading out for ever and steady motion might never be attained, but if the body were moved steadily in a direction at right angles to the axis of rotation, and if the fluid were contained between parallel planes also perpendicular to the axis of rotation, it seems very improbable that no steady motion satisfying the equations of motion could be attained. There is more chance that (*b*) may be true. A class of mathematical expressions representing the steady motion of a sphere along the axis of a rotating liquid has been obtained.‡ This solution of the problem breaks down when the velocity of the sphere becomes indefinitely small, in the sense that it represents a motion which does not decrease as the

* 'Roy. Soc. Proc.,' A, vol. 93, p. 99 (1917).

† *E.g.*, a sphere or any body except an infinite cylindrical body with its axis parallel to the axis of rotation.

‡ G. Taylor, 'Roy. Soc. Proc.,' A, vol. 102, p. 180 (1922).

velocity of the sphere decreases. It seems unlikely that such a motion would be produced under experimental conditions.

There remains the third possibility (*c*). In this case the motion would be a very remarkable one. If the liquid were contained between parallel planes perpendicular to the axis of rotation, the only possible two-dimensional motion satisfying the required conditions is one in which a cylinder of fluid moves as if fixed to the body. The boundary of such a cylinder would act as a solid body, and the liquid outside would behave as though a solid cylindrical body were being moved through it. No fluid would cross this boundary, and the liquid inside it would, in general, be at rest relative the solid body. This idea appears fantastic, but the experiments now to be described show that the true motion does, in fact, approximate to this curious type.

In these experiments, bodies were moved slowly through water contained in a rectangular tank which was rotating at a considerable speed. The stream lines relative to the rotating system were made visible by means of coloured fluid, and this was photographed by a camera placed on the axis of rotation (which was vertical) and aiming downwards through the plate-glass top of the tank. The arrangement is shown in fig. 1. In that diagram A is the tank,

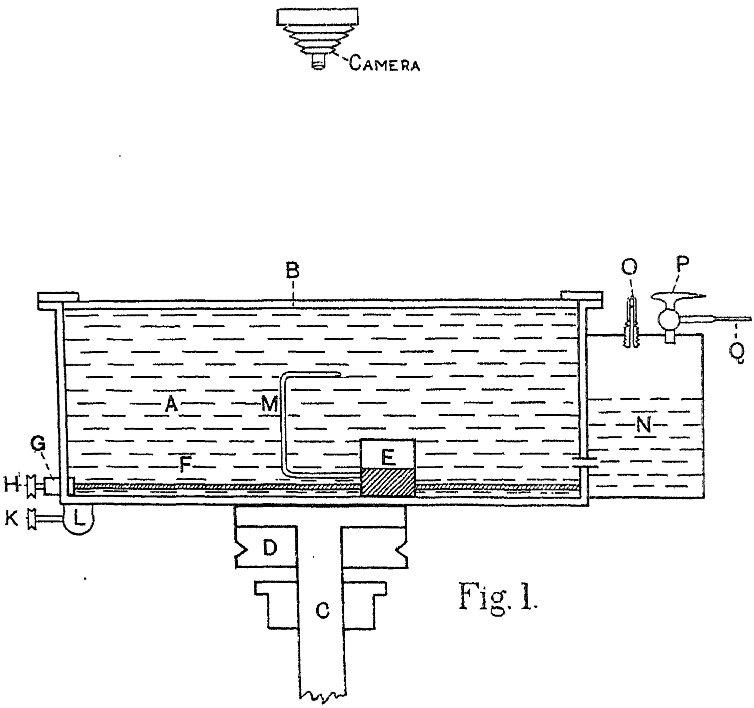


Fig. 1.

B is the removable plate-glass top which was screwed down with a water-tight joint capable of standing considerable pressure. The tank was 9 inches wide by 12 inches long and 4 inches deep. C is the vertical shaft about which the tank rotates, and D is the driving pulley. The apparatus was rotated at a uniform speed by an electric motor fitted with a governor, but this is not shown in the diagram.

Since it was necessary to give the whole system, including the water, a uniform rotation before starting the experiment, the mechanism necessary for moving the body through the water and for operating the apparatus used for making the stream-lines visible had to be fixed to the tank so as to rotate with it, but at the same time to be capable of being actuated from outside. This gave rise to the chief difficulty of the experiment. The body E (fig. 1) was moved slowly along a groove across the middle of the tank by means of a screw F of fine pitch, cut on a small steel shaft which passed through a stuffing-box G. This shaft was driven by a small motor L through two pulley wheels H and K connected by a fine endless silk thread. A small electric motor L was fixed to the under side of the tank, and was connected with a battery and switch through a wire, which dipped into a fixed annular trough containing mercury, and placed concentric with the axis of rotation.

On operating the switch while the tank was in motion, the body E could thus be made to move slowly across the middle of the tank.

To make the stream-lines visible it was necessary to have a source of coloured fluid moving with the body E. This end was attained by using the body itself as a reservoir for the coloured fluid whence it was led by a very fine metal tube M to the point at which it was desired to start the stream-line. In order to control the discharge of coloured fluid the upper part of this reservoir was filled with air, and the pressure of the water in the tank was gradually reduced while the experiment was proceeding. The reduction in pressure in the tank caused the air imprisoned in the upper part of the body E to expand and expel the coloured liquid through the tube M.

In order to get a steady stream of coloured fluid through M it was necessary to reduce the pressure in the tank at a uniform rate. This was accomplished by fixing a box N to the outside of the main tank, and the two were connected so that water could flow between them. The upper part of the box N was an air reservoir. The pressure in the tank could thus be raised by pumping air into N through a bicycle valve O which was soldered to the top of it.

In order to reduce the pressure at a uniform rate a fine capillary tube Q was fitted which allowed air to escape slowly out of N; and in order to keep

the pressure up till the coloured liquid was wanted a stopcock P was inserted between N and Q. This stopcock was operated by a spring and trigger which could be released while the apparatus was in motion.

To photograph the stream-lines several mercury vapour spark gaps of the type used by Mr. C. T. R. Wilson were arranged in series round the apparatus, and to make a good background for the coloured streaks the bottom of the tank was silvered but not polished. Eosin was used as a colouring matter, and the eosin solution was made up to the same density as water by adding alcohol.

To perform an experiment the tap P was turned off and the trigger for releasing it was set. Air was then pumped into the reservoir N till the pressure was nearly, but not quite, sufficient to burst the glass top of the tank. The screw F was then turned till the body E was at the beginning of its path. The apparatus was then set rotating and left for some minutes till it was certain that all the water had attained a uniform rotation. When everything was ready to take a photograph the spring which turned the tap P was released. Directly the coloured liquid began to appear at the end of the tube M the switch operating the motor L was closed and the body E began to move. When the body got near the middle of the tank a spark was passed through the illuminating apparatus and an exposure made. Some practice was necessary before these operations could be performed in the correct order. The essential point aimed at in designing the apparatus was attained, for the speed of rotation was high while the speed of the body through the liquid was low.

Results of the Experiments.

In the first experiments the moving body was a cylinder 1·5 cm. diameter which extended from bottom to top of the tank. The tube M (fig. 1) was arranged so that the coloured stream emerging from it struck the cylinder centrally and divided into two. For reasons explained in a previous work,* the colouring matter remains in thin sheets, which appear as thin lines when seen edgewise from a point on the axis of rotation. These lines which were very visible in the photographs showed the well-known alternate vortices which are formed behind a cylinder moving in a fluid, but it must be remembered that these lines are not stream-lines in the mathematical sense of the words when the motion is not steady.

The next experiment was made with a sphere, and the stream of coloured

* "Experiments with Rotating Fluids," 'Roy. Soc. Proc.,' A, vol. 100, p. 114 (1921).

fluid was discharged from a point in front of its centre. The coloured streaks were very similar to those obtained with a cylinder, except that the line of the wake of alternate vortices did not lie directly behind the sphere; on the other hand, increasing speed of rotation made the wake appear more and more like that of a cylinder. This experiment seems to suggest that the motion is something like that outlined in the third alternative (*c*) (p. 213), a cylinder of fluid of the same diameter as the sphere moving with it and acting towards the rest of the fluid as if it were a solid cylinder.

To test this the apparatus was arranged so that a stream-line at some height above the body E could be examined. The body E consisted in these experiments of a short cylinder, about 1 inch high by $1\frac{1}{4}$ inches diameter. This rested on the bottom of the tank, and there was thus about 3 inches of water between the top of it and the top of the tank. The coloured liquid was led by the pipe M to a level $1\frac{1}{2}$ inches above the top of the moving body. Under these circumstances the coloured liquid would, if there were no rotation, pass over the middle of the top of the body. The arrangement is that shown in fig. 1.

In the first of the experiments made with this body the coloured liquid was discharged from a point 1 inch in front of the imaginary vertical cylinder enclosing the body, as shown in fig. 1. It was found that the coloured stream flowed straight towards this imaginary cylinder to a point vertically above the foremost point of the body. At that point the stream divided as though it had struck a solid obstacle. The fact that this virtual "solid obstacle" coincided with the imaginary cylinder enclosing the body can be seen in the photograph (Plate 25, fig. 2). The point from which the coloured stream emerges is shown at A. The point at which the stream divides is marked with an arrow B. At this point part of the coloured stream passes to the right and collects in a sheath C (fig. 2) which seems to remain close to the surface of the imaginary cylinder. The rest of the coloured liquid flows round the imaginary cylinder to the left and breaks away from it, forming large eddies D. The top view of the body E can be seen in the photograph, and it will be seen that the water contained in the cylinder vertically over the body E is quite clear. The broad black line which passes under it is the driving screw F (figs. 1 and 2). This line accordingly shows the direction of motion of the body.

In order to make certain that the liquid inside the imaginary vertical cylinder enclosing the body does in fact move with it, an experiment was next made in which the coloured liquid was discharged from a point inside this cylinder.

A photograph taken under these conditions is shown in fig. 3 (Plate 25). In that photograph the end of the tube from which the coloured liquid issued is at A. It will be seen that it is almost exactly over the foremost point of the edge of the moving body E. The coloured liquid remained in a small compact mass D (fig. 3) which travelled with the body. In this experiment the discharge of coloured fluid and the motion of the body were started simultaneously at the end of the tank, which is just outside the right-hand end of the photograph. Though the point from which the coloured liquid was issuing had travelled more than half the length of the tank, none of this fluid had escaped from the imaginary vertical cylinder containing the moving body E, although it was $1\frac{1}{2}$ inches above the level of the top of E.

This result confirms and supplements the observation previously recorded* that in the case when a sphere is moved slowly *along* the axis of rotation the motion tends to become two-dimensional, owing to the formation of a cylindrical dead-water region extending above the body and moving with it. On the other hand, no theoretical work has so far given any indication as to how such a motion could be established. The calculations of Mr. S. F. Grace† on the motion of a solid sphere projected slowly in a liquid of the same density as itself, show that at one stage, at any rate, the disturbance in the surrounding fluid is greater in the region which lies above and below the sphere than it is in other directions. This may have some bearing on the subject, and it is to be hoped that some further light will be thrown on it when Mr. Grace applies his method of analysis to the case of a sphere which is constrained to move uniformly along, or perpendicular to, the axis of rotation.

These experiments were carried out in the Cavendish Laboratory through the kindness of Sir Ernest Rutherford to whom the writer wishes to express his thanks.

* *L.c.*, p. 189.

† 'Roy. Soc. Proc.,' A, vol. 102, p. 89 (1922).

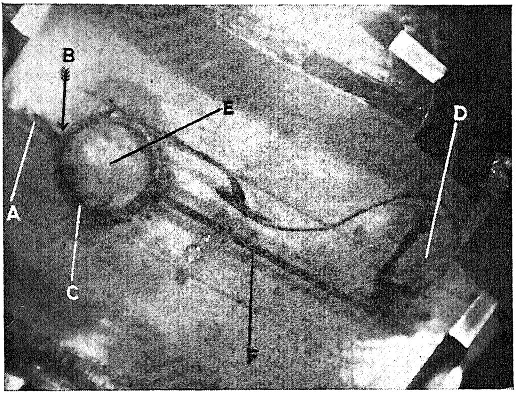


FIG. 2.

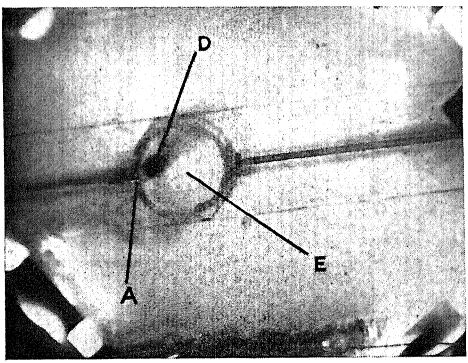


FIG. 3.

The Crystalline Structure of Anhydrous Racemic Acid.

By W. T. Astbury, B.A., A.Inst.P.

(Communicated by Sir William Bragg, F.R.S. Received June 26, 1923.)

This paper is intended to be the continuation of a previous paper on "The Crystalline Structure and Properties of Tartaric Acid" ('Roy. Soc. Proc., A, February, 1923).

Racemic acid, COOH . CH(OH) . CH(OH) . COOH, is the variety of tartaric acid which is optically inactive by "external compensation," that is, it is inactive in virtue of the fact that it consists of equal numbers of right- and left-handed molecules of active tartaric acid. It crystallises in two distinct forms, one of which is anhydrous while the other is a monohydrate. But both forms belong to the triclinic pinakoidal class of symmetry, the monohydrate growing at ordinary temperatures and the anhydrous acid above a temperature of about 70° C. This paper deals with the structure of the anhydrous form.

Crystalline Structure of Anhydrous Racemic Acid.

The observations, as in the case of Tartaric Acid, were made with a Bragg ionisation spectrometer and a Coolidge X-ray bulb of molybdenum anticathode.

Groth, "Chemische Krystallographie," p. 305, vol. III, gives the following crystallographic data :—

" Triclinic Pinakoidal. M.P. 206°. Spec. Grav. 1·783.

$$a : b : c = 1\cdot5228 : 1 : 1\cdot0250$$
$$\alpha = 82^\circ\, 20', \quad \beta = 122^\circ\, 56', \quad \gamma = 111^\circ\, 52'$$

" Scacchi obtained the anhydrous acid from aqueous solution at 73° . . .
" Always twins on b (010) with manifold and often irregular growth, frequently
" with lamellar repetition . . . . . Cleavage on c (001) and b (010), very perfect."

The crystals were grown from an aqueous solution of ordinary racemic acid (monohydrate) kept in a thermostat at 73° C. They showed a great tendency to repeated twinning on the face b (010). It was only after a large number of crystallisations that a few small untwinned crystals were obtained. These were generally combinations of a (100), c (001), and ρ (10$\bar{1}$), with occasionally μ (1$\bar{1}$0). The faces c (001) and b (010) are extremely perfect cleavages and were tested first with the spectrometer. They gave very good reflections (in fact, the reflection from (010) is enormous) corresponding to the spacings $d_{010} = 4\cdot50$ A.U., $d_{001} = 4\cdot17$ A.U.

The crystals belong to the triclinic pinakoidal (anorthic) class of symmetry,

i.e. they possess centro-symmetry only. This being so, we must expect at least two asymmetric molecules in each unit cell, the symmetry of the structure as a whole being brought about by the presence of two interpenetrating anorthic lattices, either of which is centro-symmetrical with respect to the other. And, indeed, this much is also evident from the fact that racemic acid is a combination of equal numbers of right-handed and left-handed molecules of active tartaric acid (the molecules of which we know to be completely asymmetric); in other words, it is clear from chemical experiments that the unit cell, in order to repeat through space and show the requisite symmetry, must contain, at least, one right-handed and one left-handed molecule.

In the case of tartaric acid, after placing one molecule at each of the corners of the unit monoclinic cell, it was further possible, by analytic methods, to assign some limits to the position of the second molecule. Similar methods applied to the anorthic system show that the position of the second molecule is indeterminate. For a centre of symmetry implies that to every point (x, y, z) there is a corresponding point $(-x, -y, -z)$. Consider now a structural unit at the origin of a space lattice. Let it be represented by a system of points whose co-ordinates are :—

$$\begin{array}{ccc} x_1 & y_1 & z_1 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_n & y_n & z_n. \end{array}$$

Such units, which we may call A units, are the corresponding points of one of the two interpenetrating lattices. Thus the co-ordinates of the complete system of A units may be written

$$\begin{array}{ccc} x_1 + la, & y_1 + mb, & z_1 + nc, \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_n + la, & y_n + mb, & z_n + nc, \end{array}$$

where l, m, n are integers, positive or negative.

The co-ordinates of the second (B) system of units which interpenetrates the first are centro-symmetrical with respect to the first, *i.e.* after allowing for necessary shifts αa, βb and γc parallel to the co-ordinate axes, they may be written

$$\begin{array}{ccc} -x_1 - la + \alpha a, & -y_1 - mb + \beta b, & -z_1 - nc + \gamma c, \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$$

etc.

Now, if the complete structure repeats through space and shows the proper symmetry, the same process applied to B units must necessarily reproduce A units. The co-ordinates of the new A units obtained in this way are

$$x_1 + la - \alpha a + \alpha a, \quad y_1 + mb - \beta b + \beta b, \quad z_1 + nc - \gamma c + \gamma c,$$

etc.,

i.e., $$x_1 + la, \quad y_1 + mb, \quad z_1 + nc, \quad \text{etc.},$$

from which it follows that all of the three shifts parallel to the axes are indeterminate, and the second molecule may occupy any position within the cell.

This fact adds considerably to the difficulty of locating the second molecule in the anorthic system and often forces us to rely almost exclusively on the evidence which may be derived from a study of the "habit" of crystals. We shall see below how this evidence is of supreme importance in the case of racemic acid.

Fig. 1 represents the unit cell of the anorthic system as defined by Groth.

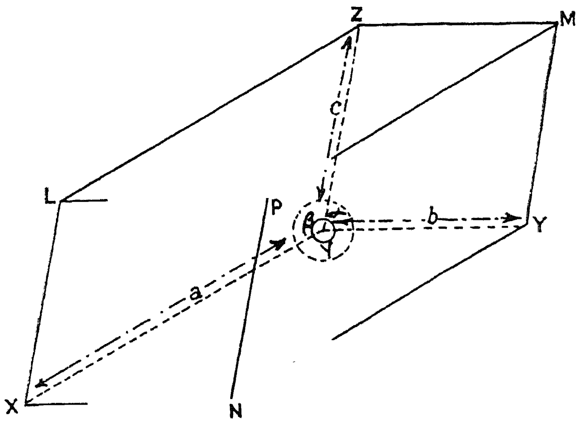


FIG. 1.

The general expression for the length of the normal d from the origin of co-ordinates to the plane (hkl) is given by

$$\frac{N^2}{d^2} = \frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma$$
$$+ 2\left[\frac{kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{lh}{ca}(\cos\gamma\cos\alpha - \cos\beta)\right.$$
$$\left. + \frac{hk}{ab}(\cos\alpha\cos\beta - \cos\gamma)\right],$$

where α, β and γ are the axial angles $\widehat{YZ}$ $\widehat{ZX}$, $\widehat{XY}$, a, b and c are the intercepts

on the axes made by the parametral plane (111), and N is given by the equation

$$N^2 = 1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma.$$

If we now assume that there are two molecules, one right-handed and one left-handed, in the unit cell of anhydrous racemic acid, as defined by Groth, we may from the above formulæ calculate the values of a, b, and c to be expected and also the spacings of the various planes. For the volume of the unit cell (fig. 1) is abcN; and thus

$$\begin{aligned} \text{Mass of anorthic cell} &= b^3 \text{N} \times 1{\cdot}783 \times 1{\cdot}5228 \times 1{\cdot}0250 \text{ A.U.} \\ \text{and also} &= 2 \times 150 \times 1{\cdot}66 \text{ A.U.} \end{aligned}$$

Whence

$$\left.\begin{aligned} b &= 6{\cdot}134 \\ a &= 9{\cdot}337 \\ c &= 6{\cdot}287 \end{aligned}\right\} \text{A.U.} \quad \text{and} \quad \left.\begin{aligned} d_{100} &= 7{\cdot}310 \\ d_{010} &= 5{\cdot}670 \\ d_{001} &= 5{\cdot}255 \end{aligned}\right\} \text{A.U.}$$

It is clear that the results of this calculation do not agree with the values of d_{010} and d_{001} obtained by experiment. There cannot then be two molecules in the " fundamental " cell chosen by crystallographers. This fact is confirmed by repeating the above calculation with one molecule per cell, when we get :—

$$\left.\begin{aligned} a &= 7{\cdot}41 \\ b &= 4{\cdot}87 \\ c &= 4{\cdot}99 \end{aligned}\right\} \text{A.U.} \quad \text{and} \quad \left.\begin{aligned} d_{100} &= 5{\cdot}80 \\ d_{010} &= 4{\cdot}50 \\ d_{001} &= 4{\cdot}17 \end{aligned}\right\} \text{A.U.}$$

These results agree with the above-mentioned observations on (010) and (001).

The results of the complete examination of the crystal are shown in Table I. The reflections are all in agreement with one molecule per crystallographic cell, with the exception of the planes (110), (310), (130), $(1\bar{1}0)$, $(1\bar{3}0)$ and $(\bar{1}1\bar{2})$. In these the observed spacing is double the calculated. Such anomalies are very simply explained if the crystallographic cell is partly built up of right-handed and partly of left-handed molecules as shown in fig. 2.

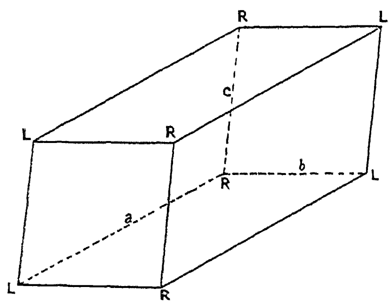


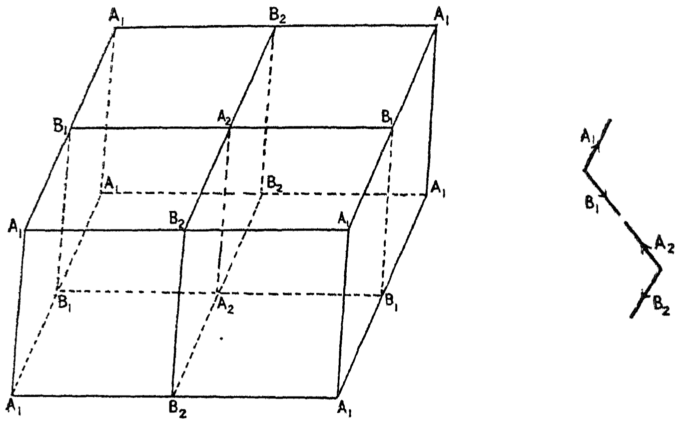
Fig. 2.

Table I.

Plane.	Spacing (A.U.)		Approximate relative intensities from successive orders.							Remarks.
	Calculated on basis of one mol. per cell.	Observed.	Different planes not strictly comparable, except to extent shown.							
			1.	2.	3.	4.	5.	7.	9.	
100	5·80	5·81	10	120	0	12				Weak.
110	3·06	6·18	200	36	4	0	0			Strong.
310	1·58	3·10	37	0						
210	2·12	2·15	0	34						
130	1·34	2·70	45	17	6					
120	1·88	1·90	54	0						
$1\bar{1}0$	4·41	8·81	200	13	140	5	26	23	3	Strong.
$1\bar{3}0$	1·60	3·24	31	0	0					
$1\bar{2}0$	2·41	2·46	13	4						
$10\bar{1}$	4·84	4·80	50	90	0	2				Strong.
$20\bar{1}$	3·39	3·41	19	22						
$30\bar{1}$	2·29	2·29	34	4						
201	1·94	1·94	13	0						
101	2·76	2·73	80	0	0					Strong.
102	1·69	1·69	6	0						
010	4·50	4·50	90	20	0					Very strong.
001	4·17	4·08	60	0	0					Very strong.
011	2·93	2·93	19	0						Strong.
$0\bar{1}1$	3·21	3·19	22	0	0					Strong.
$0\bar{2}1$	2·06	2·07	8	0	0					
$11\bar{1}$	3·01	3·01	52	35	0					
$\bar{1}1\bar{1}$	2·64	2·64	34	0						
$12\bar{1}$	1·90	1·90	36	0						
$\bar{1}1\bar{2}$	1·69	3·38	20	0						

In this arrangement each R-molecule is exactly alike and each L-molecule exactly alike, but the R's and L's are centro-symmetrical with respect to each other. Racemic acid is sometimes spoken of as though it were an inactive double molecule of weight 300, but careful examination of the evidence does *not* afford any reason for believing so. For instance, the general case of an asymmetric doublet would be represented by fig. 3, in which A_1 and A_2 are both right-handed molecules (say), B_1 and B_2 are both left-handed molecules, yet (A_1B_1) and (A_2B_2) are both asymmetrical double molecules, but so orientated as to be centro-symmetrical with respect to each other. In this fundamental cell, the co-ordinates of the four molecules may be written

$$A_1\,(000),\ B_1\left(\frac{a}{2}00\right),\ A_2\left(\frac{a}{2}\frac{b}{2}0\right)\text{ and }B_2\left(0\frac{b}{2}0\right),$$



a. *b.*

FIG. 3.

Any plane passing through the points of the lattice may then be written

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=1,$$

where (hkl) are the indices of the plane. If the plane (hkl) is interleaved half-way, the equation of such an interleaving plane will be

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=\tfrac{1}{2}.$$

In the general case, where A_1, A_2, B_1 and B_2 are all different, no plane will be exactly interleaved, but should the doublets (A_1B_1) and (A_2B_2) be not asymmetrical but centro-symmetrical, A_1 will be indistinguishable from A_2 and B_1 from B_2, and we shall find that some of the planes will be halved. The following (Table II) summarises the results of both theory and experiment.

These results show conclusively that A_1 *is* indistinguishable from A_2, and likewise B_1 from B_2; that is, if a double molecule (A_1B_1) exists, it is centro-symmetrical and indistinguishable from (A_2B_2). This is equivalent to saying that, to all intents and purposes, there are only two molecules (of weight 150) per fundamental cell, and that there is *no* evidence from X-ray and crystallographic data that racemic acid has an independent existence as an inactive double molecule of weight 300.

It is now clear that the "habit" of the crystal has deceived the crystallographer and led him to choose a cell which is not fundamental, in the sense of being the minimum parallelepiped that will repeat through space. The crystallographic cell contains two half-molecules, but the fundamental cell is built of one right-handed and one left-handed molecule. The reason for this

Table II.

I.	II.		III.	IV.	V.	VI.
Indices on Full Cell. (Fig. 3.)	Planes in which molecules lie. 1.	$\frac{1}{2}$.	Effect if $A_1 = A_2$ $B_1 = B_2$	III referred to Crystallo-graphic Cell.	Indices of IV.	Observed examples of IV. and V.
Odd odd odd	A_1A_2	B_1B_2	Not halved	Doubled	Odd odd even	$(110$ $(1\bar{1}0)$ (310) (130) $(1\bar{3}0)$, $(\bar{1}1\bar{2})$.
Odd even even	A_1B_2	A_2B_1	Halved	Normal	Odd even even	(100) (120) $(1\bar{2}0)$ (102).
Even odd even	A_1B_1	A_2B_2	,,	,,	Even odd even	(010) (210).
Even even odd	$A_1B_1A_2B_2$	—	Not halved	,,	Odd odd odd	$(11\bar{1})$ $(\bar{1}1\bar{1})$.
					Even even odd	(001) (201) $(20\bar{1})$ $(0\bar{2}1)$.
					Odd even odd	$(12\bar{1})$ (101) $(10\bar{1})$ $(30\bar{1})$.
					Even odd odd	(011) $(0\bar{1}1)$.
Odd odd even	A_1A_2	B_1B_2	,,	Doubled	Odd odd even	As above.
Odd even odd	A_1B_2	A_2B_1	Halved	Normal	Odd even even	,, ,,
Even odd odd	A_1B_1	A_2B_2	,,	,,	Even odd even	,, ,,

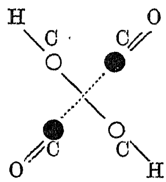
is that, as is very common in organic crystals, the best developed planes are those which contain the most molecules. Other good examples of this phenomenon are naphthalene, anthracene and tartaric acid. A careful study of the habit of an organic crystal is often of the greatest use for determining the relative positions of the molecules contained in the fundamental cell. Indeed, in many cases, the evidence afforded by the habit is much more reliable than that derived from intensity measurements, though, in the case in question, Table I shows that the most densely packed planes give rise to the heaviest reflections. But such a series of confirmatory results is by no means always obtained.

The question now arises of the orientation of the molecules in the cell and the way in which they are linked together. Since the A and B molecules are centro-symmetrical with respect to each other, any line in the A molecule must be parallel but oppositely directed to the corresponding line in the B molecule. This is the essential condition to be satisfied.

We notice first the dimensions $a = 7 \cdot 41$ A.U., $b = 4 \cdot 87$ A.U., $c = 4 \cdot 99$ A.U. of the crystallographic cell, at the corners of which we have shown the molecules to be located. This cell possesses very perfect cleavages, b (010) and c (001).

These cleavages are so easy and clear cut that they point unmistakably to the planes (010) and (001) as being planes across which there are direct molecular junctions, which can be ruptured without any such obstruction as might be caused by other molecules lying even partially in the way. In fact, they are just what we should expect in the case of a simple cell carrying one molecule at each of its corners, and so orientated as to make one half of the molecules centro-symmetrical with respect to the other half.

Again, the approximate equality of the lengths $b = 4 \cdot 87$ A.U. and $c = 4 \cdot 99$ A.U. and their size remind us immediately of the structure of active tartaric acid (*loc. cit.*). In that structure, an end view of the molecule may be represented by



and a projection of this arrangement on the (100) plane appears almost a square, in which

$$(\mathrm{O} = \mathrm{C} - \mathrm{C} = \mathrm{O}) = (\mathrm{H} - \mathrm{C} - \mathrm{C} - \mathrm{H}) = \frac{\sqrt{6^2 + 6 \cdot 2^2}}{2} = 4 \cdot 3.$$

The accepted estimates of "atomic diameters" give the lengths of $(\mathrm{O} = \mathrm{C} - \mathrm{C} = \mathrm{O})$ and $(\mathrm{H} - \mathrm{C} - \mathrm{C} - \mathrm{H})$ as $5 \cdot 6$ and $5 \cdot 0$ respectively, when the atoms are all lying in the same straight line, but the projection of the tartaric acid molecule shows shorter values than these, because neither the $= \mathrm{O}$'s nor the $- \mathrm{H}$'s stick out at right angles to the length of the molecule. It is reasonable now to conclude that what were the "diagonal" widths of the molecule in active tartaric acid have in racemic acid been rotated so as to lie approximately in the directions of the crystallographic axes b and c, and that the beautiful cleavages observed are simply across the junctions $= \mathrm{O} / \mathrm{O} =$ and $- \mathrm{H} / \mathrm{H} -$. Such cleavages would be naturally expected across these simple intermolecular junctions.

It follows now that the main length of the molecule probably lies approximately along the a-axis of the cell, the length of which is $7 \cdot 41$ A.U. The length of the molecule in active tartaric acid crystals is $7 \cdot 69$ A.U. The agreement, for as yet we have sketched out the probable orientation of the parts of the cell only roughly, seems to be more than a coincidence.

Let us consider now the remaining dimensions of the crystallographic cell (fig. 1) :—

ZX = 10·95, XY = 10·27, ZY = 6·49, OP = 6·55, LY = 9·15
OL = 6·30 ON = 7·20, OM = 7·42, ZN = 10·50, XM=13·30.

These dimensions bring home the impossibility of fitting the tartaric acid molecule into the cell in any way other than that suggested above. True, we might re-shuffle completely the arrangement of the active molecule and bring about a fit, but the result would not be in agreement with the observed properties of the crystal. We are forced to make the length of the molecule lie approximately along the *a*-axis, even though the observed length of this axis is rather shorter (3·6 per cent.) than the corresponding length in the active crystals.

In the crystalline structure of tartaric acid the four carbon atoms which form the nucleus of the molecule are arranged so as to lie at alternate corners of an oblique (monoclinic) parallelepiped, that is, they are arranged at the corners of an irregular tetrahedron. The optical properties of the acid indicate that the configuration of this central tetrahedron is fairly stable and is the basis of the dextro-rotatory power of the tartrates in solution. In view of this evidence (see "Crystalline Structure and Properties of Tartaric Acid") we are justified in assuming that this tetrahedral arrangement is maintained, at least approximately, in racemic acid. For the moment, let us fix our attention on the parallelepiped nucleus (fig. 4).

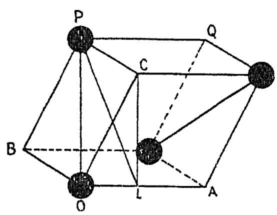


Fig. 4.

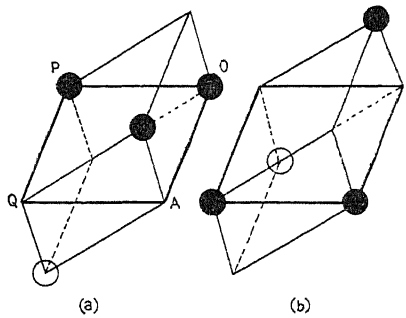


Fig. 5.

From the structure of tartaric acid it is estimated that

$$CL = 1{\cdot}16,\ \ OP = 1{\cdot}54 \ \text{ and } \ \widehat{COA} \simeq 64^\circ: \ \text{whence } \widehat{POA} \simeq 68^\circ.$$

It will be sufficient for our purpose, and in addition be easier to manipulate, if we represent the molecule by the parallelogram OPQA lying approximately

in a horizontal plane. The appearance of the nucleus is then (*a*) or (*b*), fig. 5, (*a*) being one form and (*b*) the enantiomorphous form. Consider now the face (001) into which it is clear such molecules can be fitted. It may be represented by fig. 6.

As this arrangement now stands the requirements of centro-symmetry are

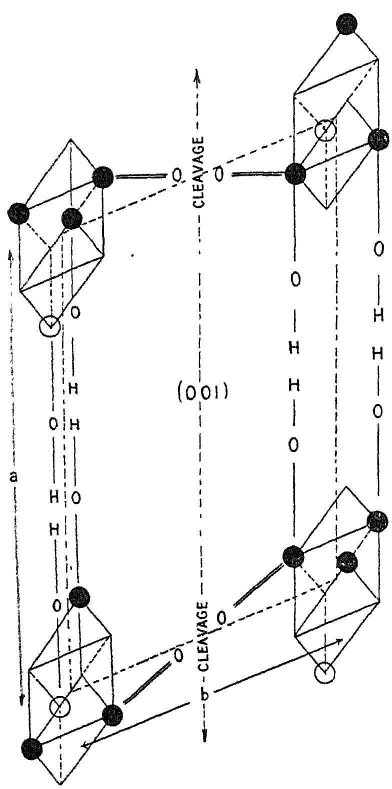


Fig. 6.

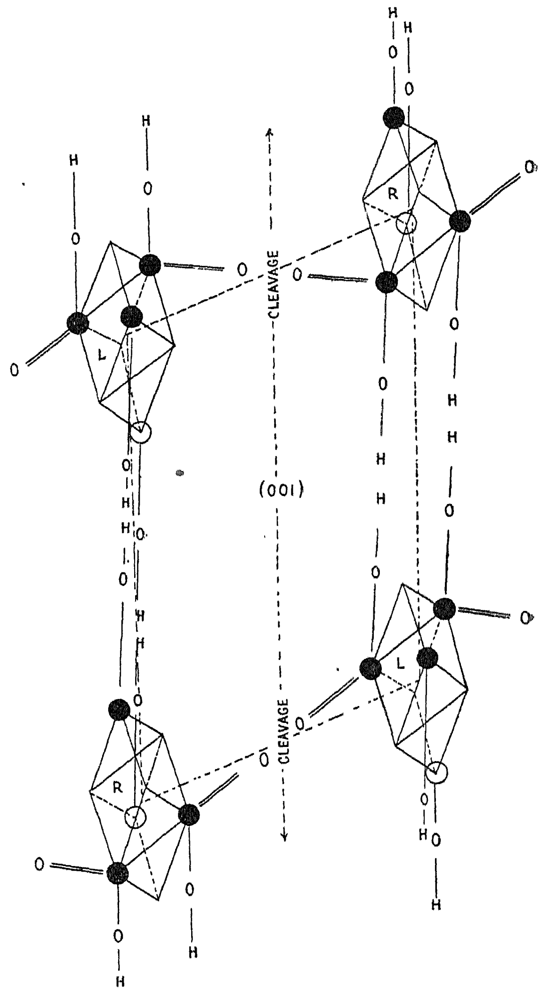


Fig. 7.

fully satisfied. Every line in a right-handed molecule is parallel but oppositely directed to the corresponding line in a left-handed molecule. Moreover, lengths occupied by similar atoms are equal with the exception of the ketonic oxygen junctions (= O / O =). These occupy different diagonals of the same parallelogram and therefore must necessarily be unequal, unless the parallelo-

gram becomes a rectangle. For this reason, the arrangement represented by fig. 6 cannot be the correct one; but it can easily be adjusted to satisfy all requirements, by a rotation in an anti-clockwise direction of the parallelogram POAQ. Symmetry demands that *all* the parallelograms corresponding to POAQ shall be rotated in the same direction to equal amounts, until the parallelogram whose diagonals are occupied by the ketonic oxygens becomes a rectangle. Thus we arrive at the arrangement shown in fig. 7.

A few points further must be touched upon. In the (001) plane shown in fig. 7 we might have taken the (— H ⁝ H —) junctions instead of the (= O ⁝ O =) junctions. The latter were decided upon from a consideration of the spectra of (001) and (010). Though that of (010) is the more intense, the chief difference

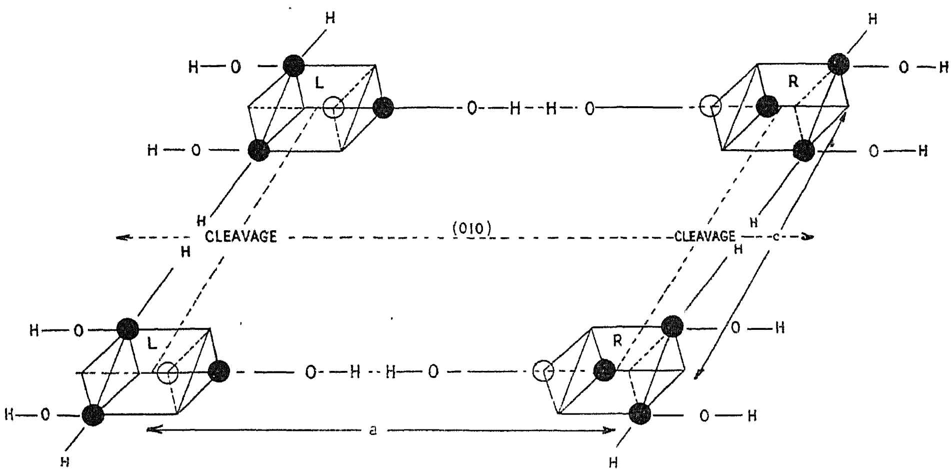


FIG. 8.

between the two lies in the fact that (010) has a definite second order whereas (001) gives nothing but a first order reflection. This observation has been taken to indicate that there is a larger mass somewhere about half-way between the (010) planes than the mass which interleaves the (001) planes. Otherwise, the arrangement in the two planes presents similar features, which undoubtedly correspond to the great similarity between the cleavages and the outstanding intensity of their reflections.

Again, by placing the (= O ⁝ O =) junctions in the (001) plane in preference to the (010) plane, we retain the peculiar shape of the carboxyl groups which was found to hold in the structure of active tartaric acid. In that structure, the ketonic oxygens are inclined at an obtuse angle to the (—COH) groups,

thus $(-\underset{\underset{O}{/\!/}}{C}-O-H)$, and it will be seen that the above structure of racemic acid emphasises the permanence of this arrangement. This is in good agreement with the chemistry of the carboxyl group, which indicates that it is a stable configuration of atoms which passes unchanged from one compound to another.

Fig. 8 shows the arrangement of atoms in the face (010). Its resemblance with the arrangement in (001) fig. 7 will be at once noted.

The Properties of Anhydrous Racemic Acid.

The crystal structure of anhydrous racemic acid described above is not only a natural deduction from that of active tartaric acid, but also it accords, in an equally satisfactory manner, with the known properties of the inactive acid.

It is remarkable how little distortion it is necessary to impress on the molecule of the tartaric acid structure in order to fit it into the racemic structure. Fig. 9

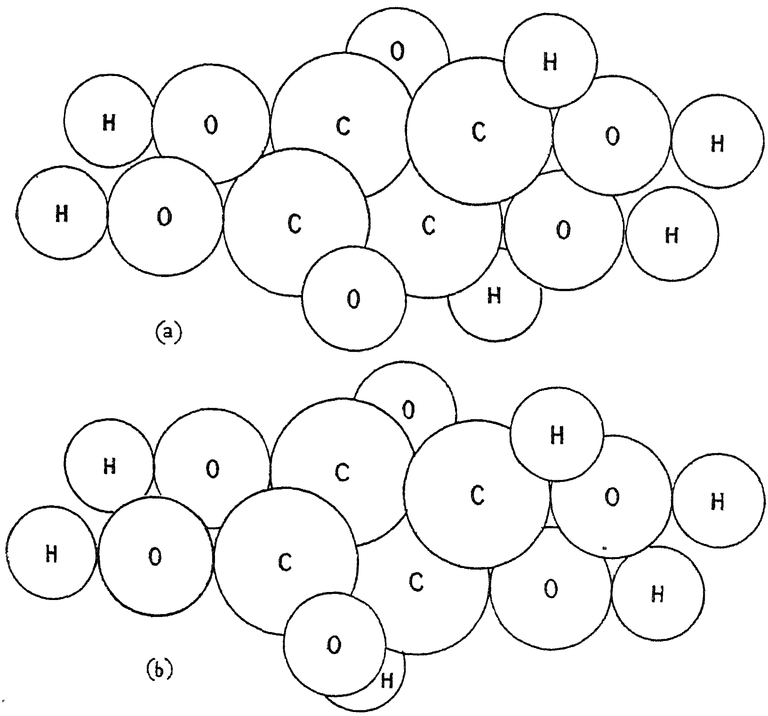


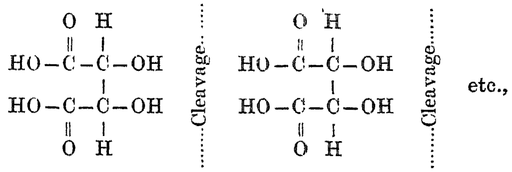
Fig 9.

shows comparative views of the two molecules (*a*) from the monoclinic crystal (tartaric) and (*b*) from the anorthic crystal (racemic). This fact constitutes

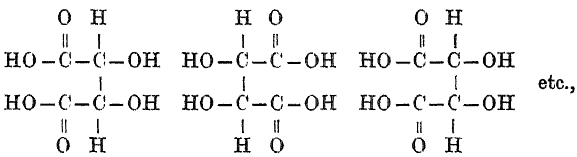
one of the strongest arguments for the general correctness of these two structures. Moreover, the atomic dimensions (with the significant excèption discussed below) are substantially the same in the two cases, for in tartaric acid it was found that the diameter of (— H) and (= O) were both approximately equal to 1 A.U., and in racemic acid the corresponding values are (— H) = 1·0 A.U. and (= O) = 1·05 A.U.

The significant change is in the length of the molecule, the a-axis in tartaric acid being 7·69 A.U., but in racemic acid 7·41 A.U. If we consider the "diameter" of carbon to remain constant (1·54 A.U.) in the two cases, this shortening of the a-axis corresponds to a decrease in the length of the carboxylic hydroxyl group from 2·5 A.U. to 2·35 A.U. Is there any simple physical change which we may associate with this contraction? Experiment shows that there is.

Firstly, it should be noticed that the molecular junction between hydroxyl groups in racemic acid is not exactly like the corresponding molecular junction in tartaric acid. The relation between the two is shown by



(*a*)



(*b*)

(*a*) representing tartaric acid and (*b*) racemic acid.

There is a good cleavage between the hydroxyl groups in tartaric acid, but in racemic acid this has disappeared. It is natural then to associate the observed contraction with the difference in the character of the two molecular junctions and the disappearance of the cleavage. There is further physical evidence which indicates a small but definite difference in the physical properties of the active and racemic acids. For instance, (1) "Mais dans ce rapprochement des deux acides (*d*- and *l*-tartaric) il s'opère un dégagement sensible de chaleur" (Biot, Rapport sur un Mémoire présenté à l'Académie par M. L. Pasteur, p. 436, vol. 29); (2) Stewart (Trans. Chem. Soc., 1907, 91, 1537)

determined the absorption spectra of aqueous solutions of *d*-, meso- and racemic tartaric acids and found that the absorption curve of the last-named began to diverge from that of the other forms at concentrations above 14 per cent.; (3) Rankin and Taylor have pointed out that in moderately concentrated solutions racemic acid has a lower viscosity than tartaric acid; (4) Dunstan and Thole (Trans. Chem. Soc. 1908, 93, 1815) have given definite evidence from viscosity measurements that racemic acid can exist to a limited extent in aqueous solution, the dissociation being nearly complete at low concentrations.

From the combined evidence of these experimental results, it is difficult to avoid the conclusion that the mixing of *d*- and *l*- tartaric acids is accompanied by a small change in the state of molecular aggregation. Such a change would be demonstrated without ambiguity only in the crystalline structure, though in strong solutions the tendency of the solute to form molecular complexes on the basis of this crystalline structure must give rise to variations, more or less appreciable, in certain physical properties of the solutions. A case in point is provided by the optical behaviour of tartaric acid solutions, the structure of the solid acid indicating a simple explanation for the anomalous properties not only of the acid solutions but also of many of the well-known tartrates (*loc. cit.*). More recently, Raman ('Nature,' March 31, 1923), from investigations of the molecular scattering of light in liquids, has adduced further evidence for this orderly association of molecules in concentrated solutions. But, indeed, the speed with which crystallisation may take place points unmistakably to such a hypothesis.

It is now suggested that the small peculiarities in the physical properties of strong solutions of racemic acid are to be ascribed solely to this tendency to form crystalline aggregates, and are to be associated with the observed contraction in the length of the molecule and the absence of a cleavage which might be expected between the hydroxyl groups.

Though the absence of this cleavage plane may at first appear strange, consideration of the melting point of racemic acid indicates clearly an unlooked-for strength in the structure, for though the melting point of active tartaric acid, which shows only one perfect cleavage, is 168°–170°, yet that of anhydrous racemic acid, showing two even more perfect cleavages, is as high as 206°. This can only mean that the third molecular junction in the latter case is of exceptional strength, and indeed favours strongly the idea of a molecular contraction as we pass from one structure to the other.

The repeated and manifold twinning of anhydrous racemic acid is a very

interesting property, which receives a ready explanation when we examine the crystal structure. The most obvious twinning is on the face (010), but it is a natural deduction from the structure that twinning on other faces is quite probable, and the phrase "manifold and irregular growth" in the crystallographic description suggests that this deduction is almost certainly correct. It is easy to see how repeated twinning on the face (010) occurs, thus :—

The plane (001) is represented in fig. 7, but we might with equal correctness have represented it by an arrangement such as the right-hand side of fig. 10, which is the reflection in the (010) plane of the arrangement in fig. 7.

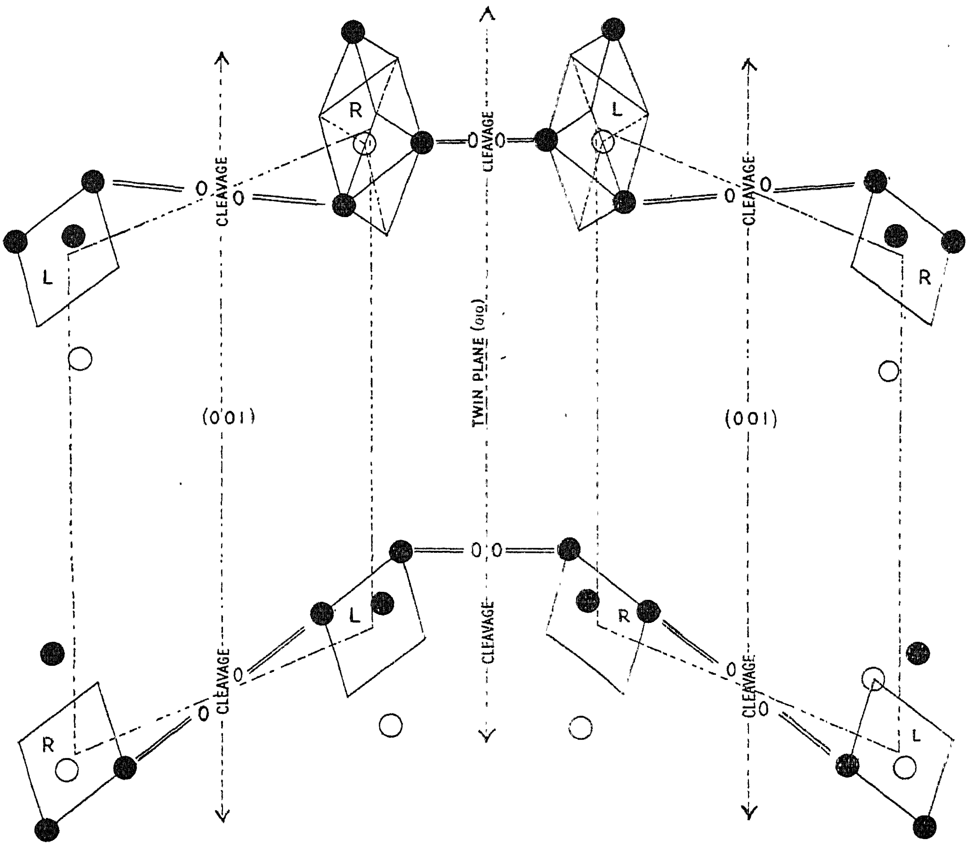


Fig. 10.

Fig. 10 represents a twin of racemic acid twinned on the plane (010). It is clear that either of the two arrangements constituting the twin is equally probable, which accounts for the fact that it is extremely difficult, if not impossible, to grow a really untwinned crystal of this substance. It is also

a natural deduction, as mentioned above, that twins similar to the one represented in fig. 10 are possible on faces other than the (010), such as the (001) and the (100), and it is almost certain that this is the explanation of the "manifold and irregular growth" which is universally observed with this crystal. For some reason, repeated twinning on (010) occurs the most frequently.

Another point worthy of mention is that the twist which is associated with the four-hydroxyl groups in active tartaric acid no longer exists in the inactive structure. The centro-symmetry demands a straightening out of these groups. And this is a very satisfactory conclusion from the point of view of the theory previously put forward to account for the anomalous rotatory dispersion of tartaric acid. In that theory, it was suggested that the arrangement of the four carbon atoms, to which is to be ascribed the dextro-rotatory power, is more or less permanent and a property of the tartrates in general, while the distortion of the hydroxyl groups is only temporary, being merely a property of the crystal structure, so that any departure from the crystalline arrangement is likely to lead to a diminution of the laevo-rotatory power. The analysis of the structure of racemic acid leads to the conclusion that the tetrahedral arrangement of the four carbon atoms must still be considered as existing more or less unaltered in the inactive structure, but that the particular arrangement of hydroxyl groups associated with the active acid has, in accordance with the previous deduction, given place to a less distorted form. In other words, the change which takes place as we pass from active to inactive tartaric acid is in effect analogous to that which must be supposed to take place on dilution or heating of the active aqueous solution. But since racemic acid is inactive by external compensation, such a change could not be detected except as a deduction from the respective crystalline structures.

Summary.

1. From observations made with an X-ray spectrometer the crystal structure of anhydrous racemic acid is obtained.

2. It is shown that the crystallographic cell is associated with only one molecule of $C_4H_6O_6$ and is not the true fundamental cell.

3. The fundamental cell is associated with one molecule of right-handed tartaric acid and one molecule of left-handed tartaric acid.

4. There is no evidence from X-ray examination that racemic acid exists as an independent inactive doublet of molecular weight 300.

5. The chemical molecule in racemic acid is substantially of the same shape and dimensions as the molecule in tartaric acid.

6. A small contraction in the length of the molecule and the absence of a certain cleavage is associated with small changes in physical properties which accompany the formation of racemic acid from its active components.

7. The disappearance of the distortion of the hydroxyl groups of tartaric acid is favourable to the theory of the anomalous optical properties of the active acid.

8. An explanation is given of the multiple twinning and irregular growth of anhydrous racemic acid.

The expenses of this research were defrayed from a grant by the Scientific and Industrial Research Department.

In conclusion, I wish to thank Sir William Bragg for the kindness and interest throughout, which has made this research possible, and also Professor A. W. Porter for his advice and helpful criticism.

The Passage of Cathode Rays through Matter.

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(Communicated by Prof. Sir E. Rutherford, F.R.S. Received May 23, 1923.)

§ 1. *Introduction.*

The pioneer experiments of Lenard* on the passage of cathode rays through matter led him to the well-known exponential law of absorption

$$I/I_0 = e^{-\lambda t}, \tag{1}$$

where I_0 is the incident, I the emergent, intensity of the beam, t the thickness of the absorbing material, and λ a constant depending upon the density of the material and the velocity of the rays. These experiments were followed up by Becker† and Leithauser‡ whose results agreed with the exponential relation, provided that I_0 was corrected for the reflected fraction of the beam.

* P. Lenard, 'Wied. Ann.,' 56 (1895).

† A. Becker, 'Ann. d. Phys.,' 17 (1905).

‡ G. Leithauser, 'Ann. d. Phys.,' 18 (1905).

The values of λ obtained by these three observers are not, however, in even approximate agreement, and owing to the slow speed of the rays employed and to experimental difficulties, their results do not appear to provide sufficient evidence for the truth of equation (1).

Whiddington* has examined the variation of λ with velocity, and shown that

$$\lambda = \frac{b}{v^4} + c, \tag{2}$$

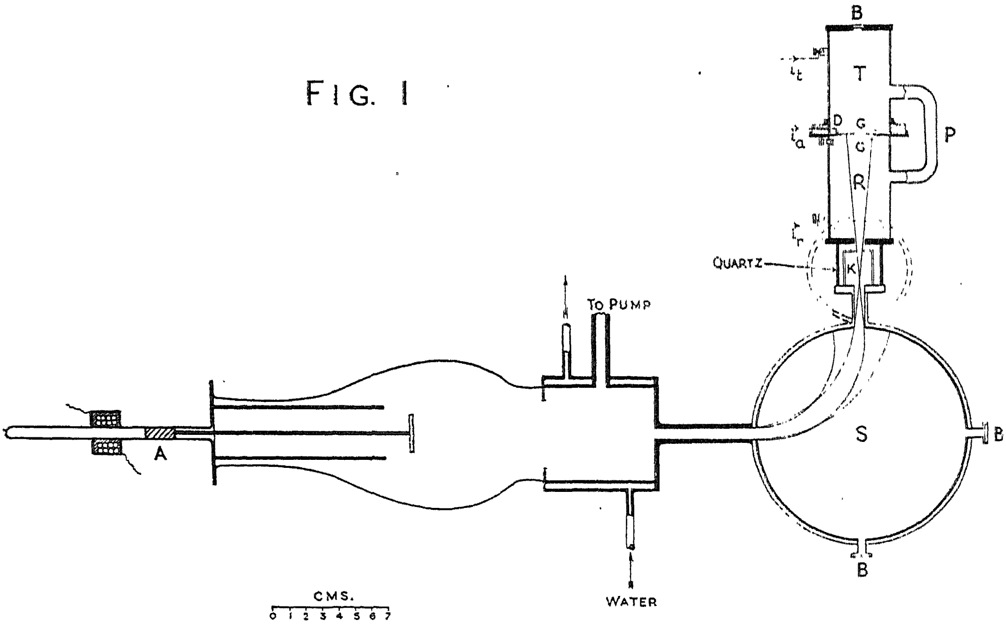
where b and c are constants. He found that (2) had only a limited validity and was unable to explain the limit on the side of higher velocity.

It seemed desirable to reopen the subject, using faster rays and more modern technique than had hitherto been employed. The experiments to be described were made with rays of velocity varying from 0·2 to 0·4 of that of light.

§ 2. *Experimental Details.*

The experimental arrangement is founded upon that of Whiddington.† Fig. 1 shows the apparatus employed. The discharge tube, constructed from a

FIG. 1



lamp-chimney, was provided with a water-cooled anode and a hardening device for the cathode. A small outside solenoid controlled the soft-iron tail A of

* R. Whiddington, 'Roy. Soc. Proc.,' A, 89 (1914).

† Whiddington, *loc. cit.*

the cathode, so that the latter could move in and out of the fixed glass shield. The potential across the tube could thus be quickly changed from 10,000 to 50,000 volts. The rays entered a solenoid S and were bent upwards to enter a special firing tube K. This was designed to eliminate soft secondary and reflected rays. Windows B served for the alignment of the beam.

The foil to be examined was placed between the two similar brass cylinders, R and T, R resting upon an insulating quartz tube. A narrow mica ring carried the foil and insulated it from R. Contact with it was obtained by two small phosphor-bronze springs (one is shown at D), carried on thin brass rods passing through the ebonite base of T. Two fine-wire grids G, of 0·4 cms. mesh, were held 2 mm. from the foil on either side by rods passing through but insulated from the cylinders.

The ebonite base of T was ground and slightly greased to give an air-tight joint with the top of R. This arrangement made the replacement of the foil a very easy matter. Changing the foil and pumping down to the necessary vacuum usually took 20 minutes with a Gaede mercury pump. A rubber tube P served to prevent bursting of the foil by inequalities of pressure.

The current in the solenoid was measured on a calibrated ammeter. The solenoid was 44 cm. long and 13·2 cm. in diameter, the calculated value of the field corrected for end effects being 10·91 gauss per amp. Direct measurements with a search coil gave a value of 10·9 at the centre and 10·5 at the sides. A value of 10·66 gauss per amp. was taken as the mean. The geometrical maximum and minimum radii of curvature were 6·85 and 6·18 cm. with a mean of 6·51 cm. A pair of compensating coils (shown dotted) served to neutralise the small stray field in K.

Two galvanometers focussing on the same scale and of sensitivity about $5 \cdot 10^{-8}$ amps. per cm. were used. A small switch-board made it possible to measure the portion of the beam transmitted (i_t), absorbed (i_a), or reflected (i_r), on one galvanometer and the remainder on the other. The fractions i_r/I, i_A/I, i_t/I, where I, the total intensity, $= i_r + i_\mathrm{A} + i_t$, were obtained by this means. The general accuracy of the galvanometer readings was 3 per cent., the tube running very steadily when taking 300 watts from a large induction-coil with a slow-speed mercury break.

§ 3. *Secondary Rays.*

Preliminary experiments showed that the current (i_A) from the foil itself decreased to zero as the velocity of the rays increased, and then grew in the reverse direction. This was evidently the result of an emission of

secondary or δ rays. A retarding field could be applied to them by means of the grids G, and their amount and energy measured.

An example is given below :—

P.D. in volts, grids to foil	0·0	—3	—6	—9	—12	—16·5	—24	—30	—48	—72	—100
Currents in foil (scale divs.)	45	45	50	54	56·5	57	57·5	58	57·5	58	58·5

Evidently the energy of these rays does not exceed 30 volts, and for the majority is lses than 10 volts.

Measurements of the ratio of the secondary to the incident intensity could not be made very accurately with the present arrangement, but definite evidence was obtained that it decreases slowly with increase of velocity of the primary rays, and that it is less for the lighter than the heavier elements. At 18,000 volts the values of this quantity for gold, silver, copper and aluminium were found to be 0·20, 0·19, 0·10 and 0·05. The above results are in accord with recent measurements by Baltruschat and Starke* which have just reached me.

To prevent secondary rays from upsetting the measurements, the grids G were kept at —100 volts with respect to the foil, so that the secondary rays were all turned back to it. Experiments showed that the grids introduced no additional complications, either by causing ionisation currents or by stopping some of the rays.

§ 4. *Variation of Absorption with Velocity.*

1. *Apparent Absorption.*—A fraction i_t/I of the rays penetrate the foil, and it is usual to measure absorption by the remaining fraction $1 - i_t/\mathrm{I}$, which includes both the absorbed and reflected rays. These measurements will be termed "apparent-absorption," to distinguish them from true absorption.

The variation of i_t/I with velocity is shown in fig. 2. The continuous curves were obtained with aluminium foils of various thicknesses—the dotted curve H is one of a number obtained with gold as absorbing substance.

It appears that for aluminium the apparent absorption $1 - i_t/\mathrm{I}$ varies as $1/v^4$ for values of i_t/I from 1·0 to 0·20. For gold, however, $1 - i_t/\mathrm{I} :: 1/v^2$. The values of the index of v found for copper and silver were 3·1 and 2·5.

The origin of this difference in the behaviour of different elements lies in the fact that apparent absorption involves both true absorption and scattering. The results of this section are similar to those found by Whiddington.† Using

* Baltruschat and Starke, 'Phys. Zeit.,' vol 23 (1922).

† *Loc. cit.*

equation (1) to find λ, he was led to express it as in (2) with the constant c largest for aluminium and equal to 0 for gold

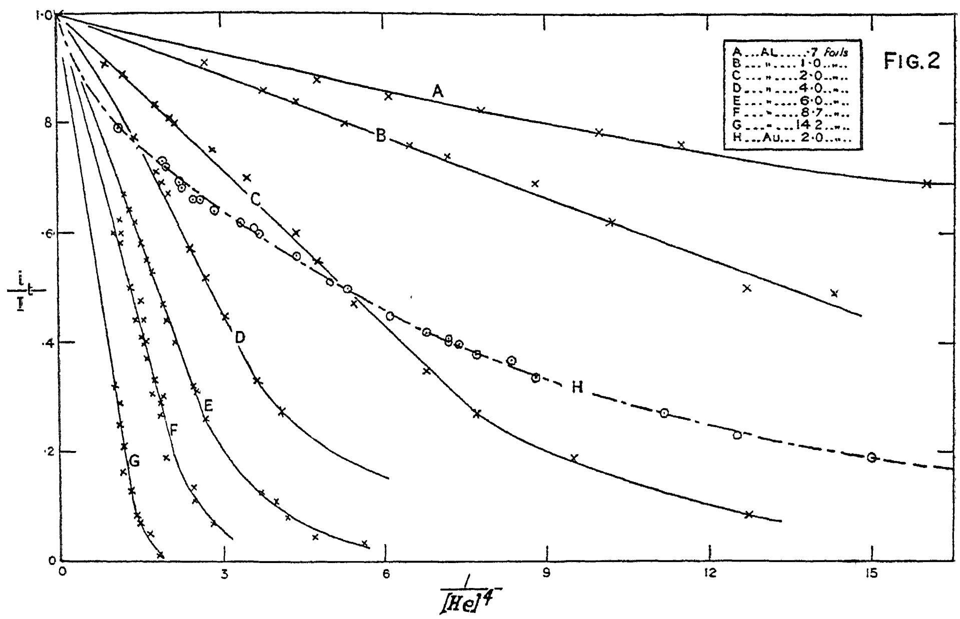


Fig. 2.—Thickness of 1 Al foil—$5 \cdot 90 \, . \, 10^{-5}$ cm. Thickness of 1 Au foil—$7 \cdot 75 \, . \, 10^{-6}$ cm.

2. *True Absorption.*—The differences noted in the behaviour of different elements in the above section disappear when the true absorption i_A/I is considered.* Fig. 3 shows four curves for aluminium and one for gold. Copper and silver gave curves of the same nature as these. The absorption —i_A/I, that is, the fraction actually absorbed in the foil—increases as I/v^4 until a critical value of the latter is reached. After this it is unaffected by any further increase in I/v^4, at any rate over a considerable region.

The constant values attained by i_a/I have been found to be due to a state of affairs where a constant fraction of the incident beam is reflected, the remainder being wholly absorbed. This result, also found by Becker,† may be compared with the measurements of Kovarik‡ and others on reflected β rays.

* The foil was insulated from the cylinders and the spring contacts D were used to pick up the current i_A due to actual stoppage of some of the rays in the foil.

† Becker, *loc. cit.*

‡ Kovarik, 'Phil. Mag.,' vol. 20 (1910).

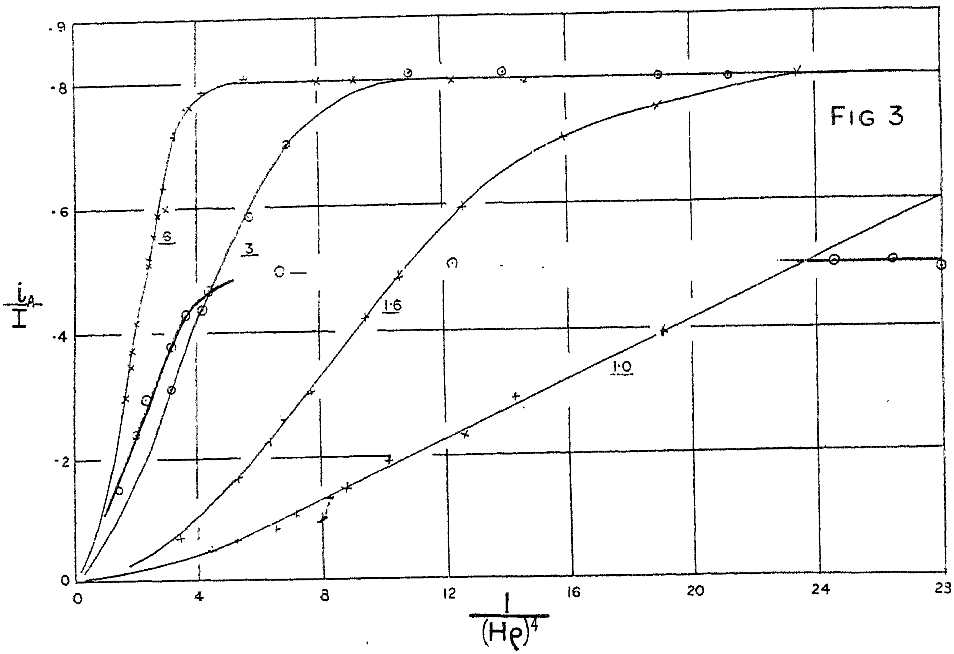


FIG. 3.—Aluminium 1·0, 1·6, 3, and 6 foils 5·9 . 10^{-5} cm. thick. Gold (thick curve) 6 foils, 7·75 . 10^{-6} cm. thick.

Table II.—Percentage reflected radiation.

Reflector.	Cathode rays (β=0·2) (Schonland).	Radium E.	Actinium D.
Aluminium	20·0	30·0	38·3
Copper	35·0	44·7	51·9
Silver	44·0	57·4	63·5
Gold	50·0	67·8	78·7

The fact that the linear portion of these curves does not pass through the origin is due to a neglect of relativity considerations, which should enter at the higher speeds.

§ 5. *Variation of Absorption with Thickness.*

The curves discussed above enable further curves to be constructed giving the variation of absorption with thickness for any constant velocity of the rays.

1. *Apparent Absorption.*—Four such curves for aluminium are shown in fig. 4. The relation is a linear one for this element over a considerable range.

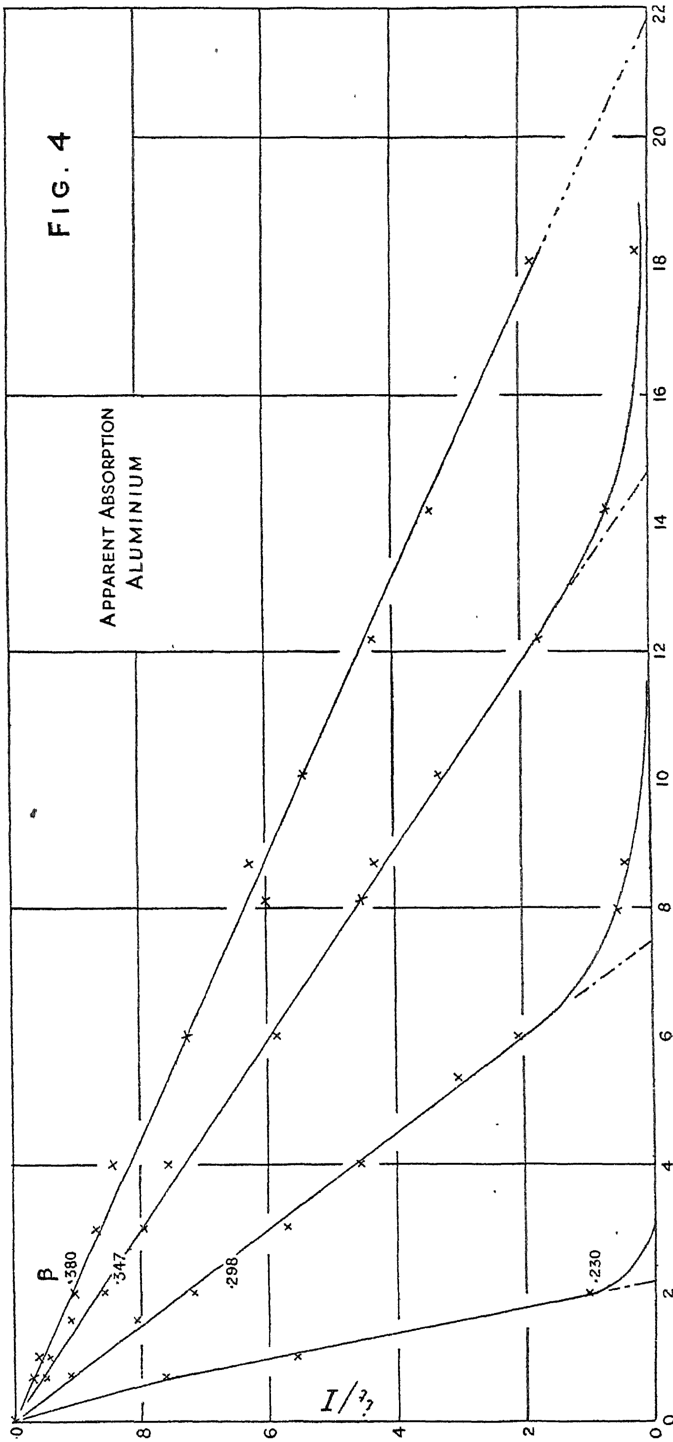


FIG. 4
APPARENT ABSORPTION
ALUMINIUM
FOILS
β
·380
·347
·298
·230
0 2 4 6 8 10 12 14 16 18 20 22
·0 ·8 ·6 ·4 ·2 0

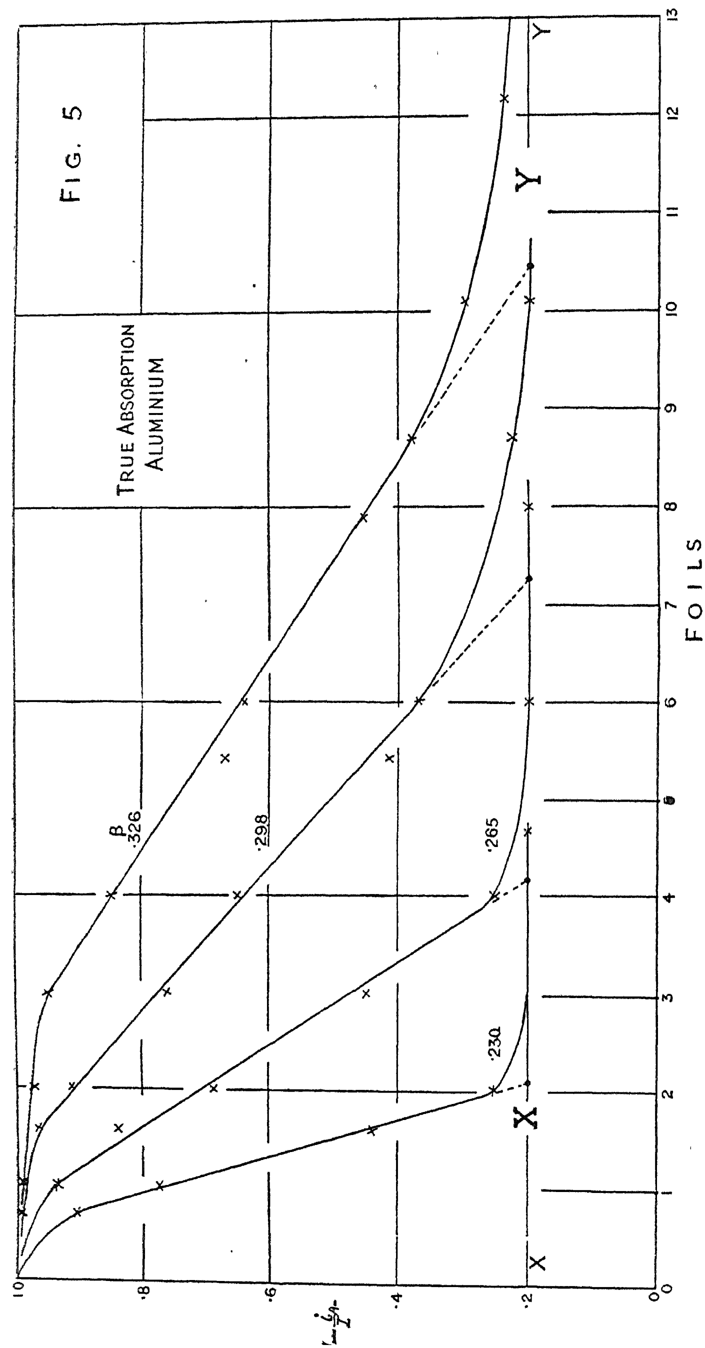


Fig. 5
True Absorption
Aluminium
β
·326
·298
·265
·230
X
Y
Foils
0 1 2 3 4 5 6 7 8 9 10 11 12 13
1·0
·8
·6
·4
·2
0

By producing the linear portion to cut the axis we obtain the " range " of the rays in aluminium for a given velocity.

Aluminium and gold were the only elements obtainable in sufficiently thin foils to examine in this way. Three curves, C, D and E, for gold are shown in fig. 6. For this element the curves are convex to the origin and no definite " range " can be obtained by this method.

These results are in striking agreement with those of Varder* on the absorption of β rays. He found a linear relation for aluminium, from which he was able to measure the range, while for platinum he obtained curves similar to those for gold in fig. 6.

2. *True Absorption.*—In fig. 5 the variation of true absorption with thickness is shown for rays of various velocities in aluminium. For all the elements examined these curves were of the same general form, as may be seen from the two upper curves A and B for gold in fig. 6. The first part of the curve is flat, the absorption then increases rapidly with thickness, finally reaching the constant value already described.

The shape of the curve is similar to that obtained by Geiger† for the decrease in the number of α rays in a beam with the thickness of air traversed. By continuing the second portion of the curves to cut the line XY we obtain the range. Since this method of finding the range is essentially different from that already described it is interesting to compare the values obtained.

$\beta = v/c$	Range [Aluminium foils].	
	By apparent absorption.	By true absorption.
0·380	21·8	—
0·347	14·8	—
0·326	10·8	10·7
0·298	7·45	7·40
0·265	4·25	4·20
0·230	2·15	2·20
0·198	—	1·60

The agreement is very satisfactory.

§ 6. *Variation of Range with Nature of Absorbing Material.*

It has been seen that the curves for true absorption are of the same nature for all the elements examined. For this reason it is possible to compare the ranges in different materials. Some results are tabulated below.

* Varder, 'Phil. Mag.,' vol. 29 (1915).

† Geiger, 'Roy. Soc. Proc.,' A, vol. 83 (1910).

Table IV.

	28,500 volts.			23,600 volts.			18,500 volts.		
Element.	Range R.	R×N	R×d	Range R.	R×N	R×d	Range R.	R×N	R×d
	cm.			cm.			cm.		
Aluminium	$6.4.10^{-4}$....	8·3	1·70	$4.36.10^{-4}$	5·7	1·16	$2.5.10^{-4}$	3·3	6·6
Copper	$1.97.10^{-4}$	8·0	1·76	$1.27.10^{-4}$	5·2	1·13	—	—	—
Silver	—	—	—	—	—	—	$6.16.10^{-5}$	2·9	6·4
Gold	$8.7.10^{-5}$	6·9	1·70	$6.2.10^{-5}$	4·9	1·19	$3.4.10^{-5}$	2·7	6·6

The table gives results for three different velocities. The first columns give the range in the element considered, the second the range multiplied by the atomic number N, and the third the range multiplied by the density of the material. It will be seen that R × N decreases with increasing N, while R × d is constant.

§ 7. *Theoretical Considerations.*

Mention has already been made of the similar character of the "apparent-absorption"-thickness curves for cathode rays and for β rays as investigated by Varder. Bohr* has given a quantitative explanation of Varder's results. He showed that the range of β rays in matter would be given by :—

$$R = (K/\Sigma)\,A \qquad (3)$$

where R is the range in cms.,

K is a constant,

A is $[(1-\beta^2)^{\frac{1}{2}} + (1-\beta^2)^{-\frac{1}{2}} - 2]$,

and Σ an expression which increases slowly with increase of velocity. In the present experiments A is approximately $\beta^4/4$.

Thus R/A should decrease slowly with velocity. The values of R/A for aluminium obtained with cathode rays are shown in column 5 of the following table, as well as some of Varder's for the β rays. Column 6 gives the values calculated from Bohr's theory.

* Bohr, 'Phil. Mag.,' vol. 30 (1915).

Table V.

(1) $H\rho$	(2) β	(3) A	(4) R gms./cm.²	(5) R/A obs.	(6) R/A calc.	
342	0·198	0·000402	0·000250	0·62	0·60	
372	0·214	0·000554	0·000336	0·61		
401	0·230	0·00078	0·000375	0·48		
465	0·265	0·00128	0·000664	0·52		Cathode rays.
527	0·298	0·00215	0·00117	0·55	0·55	
583	0·326	0·00314	0·00169	0·54		
627	0·347	0·0041	0·00232	0·57		
694	0·380	0·0061	0·00341	0·56		
	0·752			0·37		
	0·831			0·35	0·42	β rays.
	0·948			0·30	0·38	(Varder)
	0·981			0·28		

From these results and those of § 6 we may therefore say that for cathode rays of given velocity the range in any element is given by

$$R = 0\cdot 57 \times A \text{ gms./cm.}^2,$$

or approximately $R = 0\cdot 14 \times \beta^4$ gms./cm.².

Bohr also showed that the effect of large-angle scattering by the nuclei of the atoms encountered would give rise to curves such as C, D and E, in fig. 6, in the case of the heavier elements. For these elements there is still a "range," but the nuclear scattering effect prevents any accurate measurement being made from the apparent-absorption curves. This effect is also responsible for the differences, considered in section 4, in the variation of apparent absorption with velocity for different elements.

Varder's remark, "If we had no scattering or straggling we should expect to have a curve similar in shape to a Bragg α-ray curve," may be compared with the measurements of true absorption in section 5, which fulfil this expectation.

In Bohr's equation (3), the atomic number N enters into the expression for Σ together with the characteristic frequencies of the electrons in the atom. An accurate evaluation of Σ for a heavy element like gold is not at present possible, but Bohr states that a variation of Σ making the range proportional to the reciprocal of the density is probably correct, as in Table IV.

The constancy of the fraction of an incident cathode or β-ray beam which is reflected from sufficiently thick foils may be explained as follows: The fraction reflected, being due to scattering, will increase as the thickness of the material increases, until this is equal to the range of the particle. No further

increase in thickness will change the average number of nuclei encountered by a particle, and the scattering or reflection will now be constant. A variation

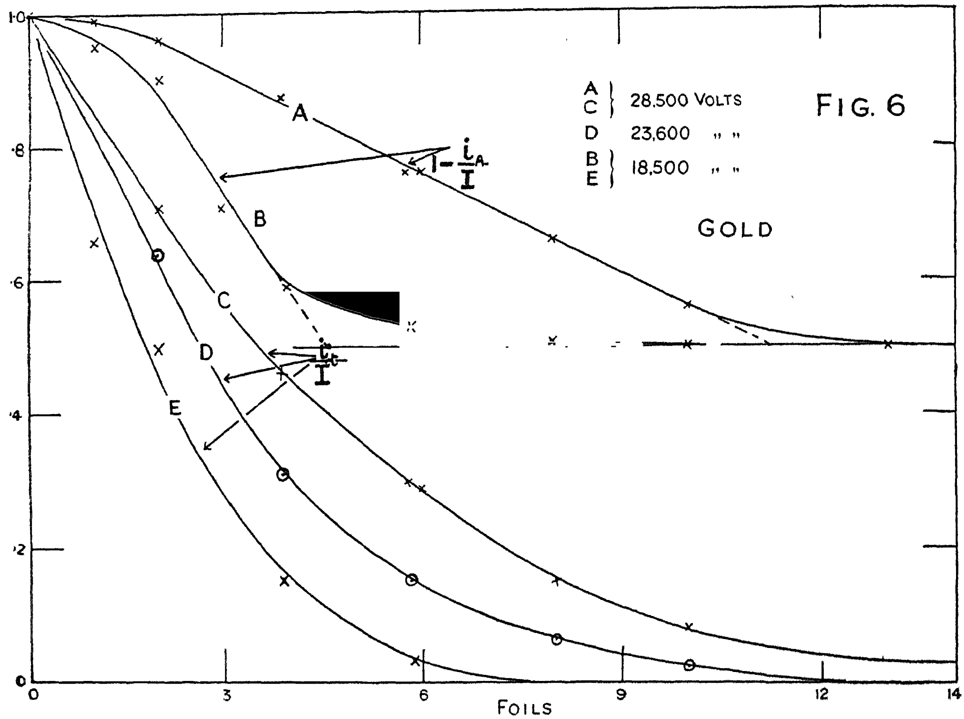


FIG. 6

in velocity will alter the range and therefore the number of atoms encountered, approximately as v^4 or (A). The inverse square of the kinetic energy varies as I/v^4 neglecting relativity. Thus the fraction scattered back, depending upon the product of these two quantities, will remain constant. The slow increase of this fraction with velocity, exhibited by Table II, requires further consideration. (*See* Note added below.)

While the present experiments are in good accord with the theory of Bohr, which is supported by a number of investigations with both α and β rays, the theory is based on a gradual loss of energy from the moving particle by collisions with the electrons encountered. This is calculated in terms of their characteristic frequencies. The possibility of a treatment based on quantum conceptions of energy interchange, as recently developed by Henderson,* should, however, be kept in mind.

* Henderson, 'Phil. Mag.,' vol. 44 (1922).

Summary.

1. The absorption of cathode rays of velocity $6.0.10^9$ to $1.2.10^{10}$ cm./sec. in various metals has been studied with an arrangement designed to eliminate interference from secondary rays, and to measure both the fraction of the beam passed through and that actually absorbed in the foil.

2. The latter fraction varies with thickness and velocity in the same manner for all elements; the nature of the variation of the former depends upon the absorbing material.

3. The conception of a range for these particles is established by two independent methods of measurement.

4. The results are explained by applying the theory of absorption due to Bohr, with which they are in quantitative agreement.

I wish to thank Sir Ernest Rutherford for his interest in these experiments, Prof. A. Ogg, of this University, for his generous help, and Mr. J. Linton for his skilful aid in the construction of the apparatus.

[*Note added, July* 17, 1923.—I have recently succeeded, with cylinders of a different design, in reducing this scattering to one-fifth of its maximum value, by the employment of fast rays and thin foils. The results of the present paper have also been confirmed within 2 to 3 per cent. with the new arrangement.]

A Flicker Type of Photo-electric Photometer giving High Precision.

By G. M. B. Dobson, M.A., Lecturer in Meteorology, University of Oxford.

(Communicated by Prof. F. A. Lindemann, F.R.S. Received June 14, 1923.)

There are numerous types of photometer, designed either to measure the relative intensities of two light sources or the "densities" of filters or photographic plates. In the bulk of these, an estimate has to be made by eye when two illuminated areas are equally bright, and this limits the accuracy which may be obtained to a probable error of about 1 per cent. for one observation.

In recent years the photo-electric cell, with one of the alkali metals as cathode, has come into use. One great advantage is that all eye estimates of brightness are avoided, and the light is given by the reading of a galvanometer or electrometer. In the usual form, when employed to obtain the densities of filters or photographic plates, the image of a constant source of light is thrown on to a small aperture covered by the plate in question.* The transmitted light falls on a photo-electric cell behind the aperture, and the current is measured by a galvanometer. To obtain the "density" of the plate from the galvanometer reading, the plate is removed and, say, a standard neutral optical wedge is placed over the aperture and adjusted until the same galvanometer reading is obtained.

The density of the plate is then the same as that of the neutral wedge at the part through which the light is passing.

The writer has had an instrument of this type in regular use for about two years, and the results have been fairly satisfactory, provided great care was taken that everything should remain constant in the apparatus between the interval when the "plate" and "wedge" were placed in the apparatus. Frequently, where a large number of readings have to be taken, it is almost necessary to take many galvanometer readings, and then convert these to

* When much light is scattered by the plate or filter being measured, an opal glass should be placed in contact with the plate on the side towards the lamp, but this reduces the light very seriously. Also it must be remembered that these photo-electric cells are only sensitive to a limited part of the spectrum, so that special precautions must be taken if the plates or filters have appreciable colour.

densities by inserting the standard wedge afterwards. Thus very great care is necessary to ensure that the light source, and the voltage on the photo-electric cell, are constant; and even with fairly elaborate precautions a considerable amount of time was occasionally wasted when it was found that one or other had varied during the series of measurements.

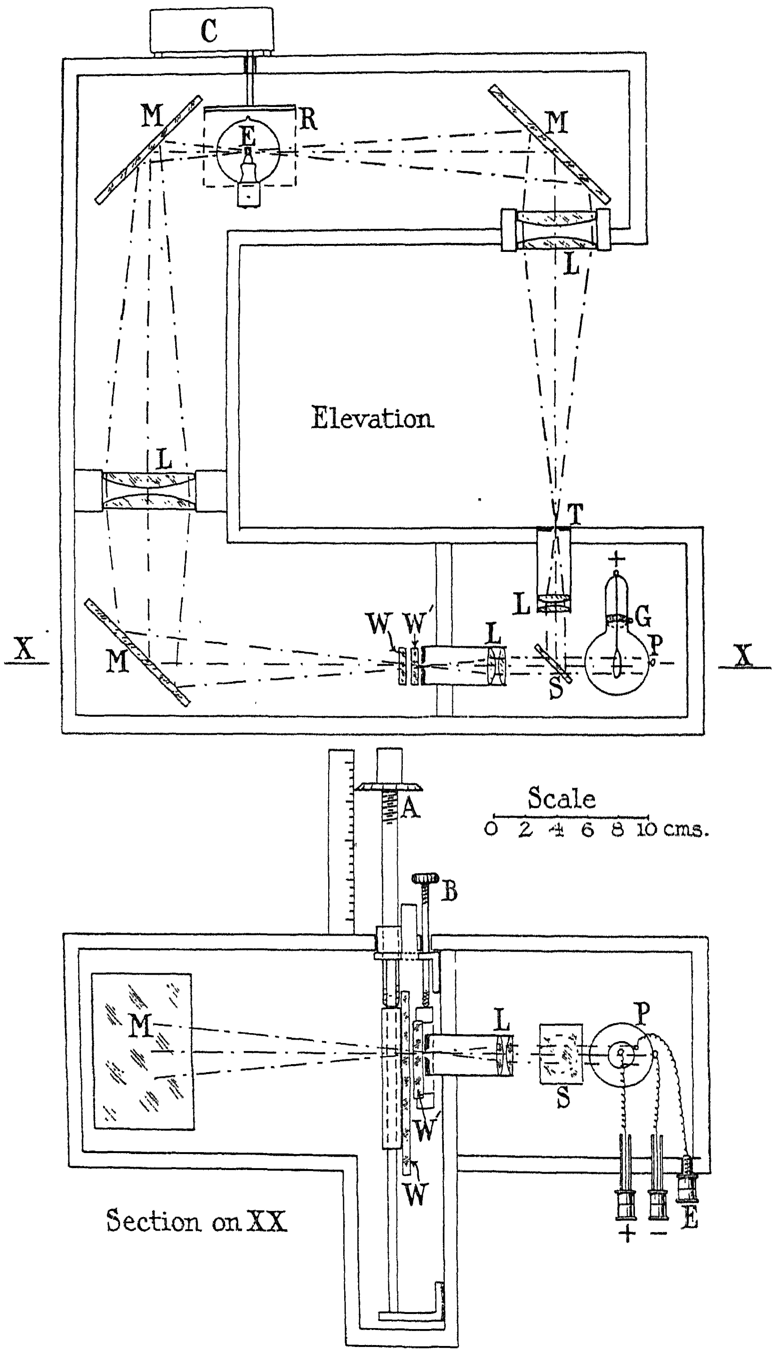
Another serious disadvantage is that when large densities are to be measured, the galvanometer deflection is small, and the percentage accuracy is not good. Thus, with densities greater than $1 \cdot 0$* the accuracy is poor, though for smaller densities, provided everything remains constant, a probable error of $\frac{1}{4}$ per cent. to $\frac{1}{2}$ per cent. should be obtained. Lastly, since it is necessary to make two measurements (one on the plate and one on the standard wedge) to obtain one density the time taken is longer than might be desired.

In view of these three objections to the ordinary simple type of photo-electric photometer, another instrument has been made here which proves to be very much superior in every way. The general principle will be easily seen from the figure below. Two beams of light are taken from an electric lamp having a small compact filament. Both beams fall on the photo-electric cell after traversing different paths, one having passed through the plate whose density is to be measured, and the other through an adjustable standard optical wedge. A shutter revolving round the lamp shuts off each beam alternately, so that in general when the light traversing the two paths is different the galvanometer will be continually oscillating. If the wedge be adjusted until there is no oscillation the light traversing the two paths will be equal. A second short wedge (placed in the reverse direction to the main wedge) allows preliminary adjustment to be made so that the two beams are equal when, say, the main wedge is in the zero position and there is no plate in the other path.

As in the older instrument, an image of the lamp is thrown on to a small aperture and the plate to be measured is placed against this. The standard wedge is moved along by a standard millimetre screw with divided head, so that its position can be very accurately measured.

The apparatus is made very sensitive, so that for small densities only a faint light is necessary; while for large densities the same galvanometer deflection is obtained merely by increasing the light by an adjustable resistance. Further, with this method of working it is quite unnecessary that the zero position of the galvanometer should appear in the field of view, so that to obtain sensitivity it may be a long way out of the field. Actually, in order

* Density is usually defined as equal to $\log_{10}$ (incident light/transmitted light).



F. Filament of electric lamp; R. Revolving shutter; C. Clockwork driving shutter; M.M. Mirrors; L.L. Lenses; S. Semi-transparent mirror; P. Photo-electric cell; G. Guard ring of cell; W. Main optical wedge; A. Controlling screw for W.; W′. Subsidiary optical wedge; B. Controlling screw for W′.

to obtain high sensitivity and a quick period, a fibre electrometer and large resistance* (about 10^9 ohms) is used instead of a galvanometer.†

It is necessary that the shutter revolving round the lamp should be accurately made, so that there is the minimum possible flicker in changing from one beam to another. In this instrument a speed of revolution of one to five per second was found satisfactory.‡

It will be seen that all the objections to the older form of instrument have been eliminated. The density is obtained in one operation. It is not necessary that the light or potential on the photo-electric cell should remain accurately constant. Large densities are measured with exactly the same accuracy as small densities. Finally, since the total galvanometer or electrometer deflection can be many times greater than the actual field of view, great accuracy can be obtained. If the revolving shutter is well made, so that it introduces negligible flicker itself, readings can be easily obtained with a probable error of 1/10 per cent. for one observation.

Summary.

A type of photometer for measuring the densities of photographic plates, etc., is described, employing a photo-electric cell and the "flicker" principle. The advantages of this type are that all densities can be measured with equal and very good accuracy—the probable error of one observation being about 0·1 per cent. The readings are quickly obtained, and no elaborate precautions are necessary.

* In some cases it might be more convenient to use valves to amplify the current and a relatively insensitive galvanometer.

† The writer is indebted to Prof. Lindemann, F.R.S., and Mr. T. S. Keeley for the loan of a particularly convenient and sensitive form of electrometer with quick period.

‡ Mr. N. V. Sidgwick, F.R.S., suggested that the shutter might be worked by hand or by a foot pedal. This arrangement was also tried and found very satisfactory.

Measurements of the Sun's Ultra-Violet Radiation and its Absorption in the Earth's Atmosphere.

By G. M. B. Dobson, M.A., Lecturer in Meteorology, University of Oxford.

(Communicated by Prof. F. A. Lindemann, F.R.S. Received 20 June, 1923.)

1. It is now well known that a connection exists between the variations in solar phenomena and changes in terrestrial weather. Thus the occurrence of an eleven-year cycle in the earth's temperature, rainfall, etc., which is coincident with the eleven-year period of sunspots has long been recognised. More recently a marked connection has been found between the irregular short-period variations also. In this connection the work of H. H. Clayton, of the Argentine Meteorological Service, may be particularly mentioned. He has found that a very definite connection exists between the variations of the "solar constant," as measured by the Smithsonian Astrophysical Department, and the temperature and rainfall some few days later in South America. The causes which lead to this connection are at present not known, though various theories have been proposed. For example, it has been suggested that the short wave-length radiation from the sun will produce ozone from oxygen in the upper atmosphere, and owing to the absorption bands of ozone both in the infra-red and ultra-violet, a change in the amount of this gas might change the radiation equilibrium temperature of the upper atmosphere, and so affect the pressure and temperature of the air below.

The measurements of ultra-violet radiation made during "solar constant" determinations by the Smithsonian Institute are very uncertain, owing to the relatively small energy in this part of the solar spectrum, and the large errors due to stray light in the spectrometer. Since the measurements here described were started, Fabry and Buisson have published measurements of the amount of ozone in the atmosphere—measured spectroscopically—but only for about a dozen days.

2. *Object of Work.*—The object of the present work was to obtain, if possible, a long series of measurements of the ultra-violet light radiated by the sun, the atmospheric transmission coefficient for this light and also the amount of ozone in the atmosphere. In addition, it was intended to measure the variations in brightness across the sun's disc for light of this short wave-length. It was hoped to correlate the variations observed with variations in terrestrial

weather. It was realised at the outset that the climate of England was very unsuitable for such measurements, and while the first part of the year was quite good, the very wet and cloudy summer and autumn prevented even as good a series being obtained as was expected.

3. *Methods of Observing.*—In order to simplify the apparatus by avoiding the use of a spectrograph, Prof. Lindemann suggested the use of a silver filter (which is transparent for light of wave-length between 3150 to 3200 Å), together with the method of photometry described below. This transmission band of silver is near the limit of the solar spectrum as received at the earth's surface, and is just within the great ozone absorption band.

To obtain the atmospheric transmissions coefficient, photographs of the sun were taken through a silver screen for various altitudes of the sun, and the intensity of the sunlight was obtained by comparing the blackness of the images of the sun with the blackness of the image of an Ilford optical wedge illuminated by a standard lamp, which was photographed on to every plate. Comparison of the blackness of the photographic images was made with the aid of a potassium photo-electric cell and galvanometer. The logarithm of the intensity of the sunlight of any one wave-length when plotted against the secant of the sun's zenith distance (sec Z) should give a straight line if the transparency of the atmosphere remains constant. The extrapolated value of the intensity at sec $Z = 0$ will give the intensity of sunlight outside the earth's atmosphere, and the slope of the line will give the atmospheric transmission coefficient.

4. *Apparatus.*—A small telescopic camera was built with quartz lenses which threw an image of the sun, 27 mm. in diameter, on a photographic plate. Immediately behind the object glass (5 cm. diam. and 40 cm. focal length) was placed the silver screen made of a series of silvered quartz plates. (The short-focus lens had a focal length of 2·5 cm.) A shutter was also provided which could be worked either electrically or by hand. Six different photographs of the sun could be taken on one plate. To test that no visible light was transmitted, the telescopic camera was placed in a dark-room with an "over-run" half-watt electric bulb inside the camera. No light whatever was seen in looking at the object glass. Or if pointed directly at the sun. no light was seen when the eye was placed at the focus of the object glass.

Outside the camera was a view-finder, consisting of a rough telescope throwing a large image of the sun on a white screen (A) on which was a circle equal to

the size of the image of the sun. During an exposure the sun's image was kept steadily on this circle. At the focus of the object glass of the view-finder was another white screen (B), having a small hole through which the sun's rays passed to the short-focus lens which formed the enlarged image on the white screen (A). Thus, on screen (B) was seen an image of the sky surrounding the sun, but without the dazzle from the bright image of the sun. This was very useful for seeing small clouds, which might otherwise have crossed the sun during an exposure, as these, of course, showed up brilliantly when so near the sun.

An adjustable bubble level and scale on the outside of the camera allowed the secant of the sun's zenith distance to be easily read at each exposure. The whole camera was fixed on a rough alt-azimuth mounting, and was kept pointing at the sun by hand. No difficulty was found in keeping the camera sufficiently steady in this way except on very windy days.

One set of observations consisted in taking six (if possible) photographs of the sun while its altitude was changing rapidly, either rising or falling. These were timed so that sec Z changed approximately the same amount between each exposure. An exposure of 120 seconds was always made. All photographs were taken from Boar's Hill, Oxford.

After taking the photographs of the sun, the plate was placed immediately behind an Ilford optical wedge, having one reference line at the "thin" end and illuminated by a white screen, itself illuminated by a 12-volt half-watt electric lamp, run just below its normal voltage (to prevent any blackening of the bulb, etc.). The plate was again exposed for 120 seconds. Thus, on one plate were obtained six images of the sun at various values of sec Z, and down the centre of the plate the image from the standard wedge.

The comparison of the blackness of the images was made with the aid of a potassium photo-electric cell. In a closed box at the top of the apparatus was a 12-volt half-watt bulb having closely coiled filament run off a constant voltage. An image of the filament was thrown by a large lens in the bottom of the box on to a small hole in a brass cap in the top of another box below. Within the lower box was a potassium photo-electric cell. The plate was placed film-down on a mechanical microscope stage above the lower box so that it was just clear of the hole in the brass cap.

A small battery of 120 to 160 volts supplied current for the photo-electric cell, and the current was measured by a string galvanometer.

To measure the blackness of the sun's images, galvanometer readings were taken with the light passing through definite parts of the sun's images. The

light was always adjusted so that when passing through the clear glass, close to the image which was to be measured, a constant galvanometer reading was given. After this, the image of the wedge was placed under the light, and the position noted which gave the same galvanometer reading as each position of the sun's images. The reading of the wedge (distance from reference line) thus obtained is a definite measure of the brightness of the sun's image, being proportional to the logarithm of the intensity of the sunlight. The blackness of the image could be measured with an accuracy of about 1 per cent.

Next, the logarithm of the intensity (in arbitrary units) of sunlight at a fixed distance from the centre of the sun's disc was plotted against sec Z. On a good day the dots lie very well on a straight line. The line extrapolated to sec $Z = 0$ gives the intensity of sunlight outside the atmosphere (I_0) and its slope gives the absorption coefficient of the atmosphere (α) (see fig. 1).

The most suitable photographic plate to use was chosen with care. Lord Rayleigh* had shown that a similar method of measurement often led to irregular results unless the film was made on "plate" glass. The only apparent effect of this is to get a more uniform thickness of film. Now it is easily seen when the film is wet that nearly all the grains due to light are within the first quarter of the thickness of the film (in the case of the fairly faint images used), while grains due to chemical fogging seem equally spaced throughout the thickness of the film. It was, therefore, suspected that Lord Rayleigh's irregular results with ordinary glass were due to grains produced by chemical fogging. Plates and developers were therefore tested for absence of chemical fog, and Ilford rapid panchromatic process plates were found to be very good, using Azol or Centinol developer. (A panchromatic plate is desirable, since very different wave-lengths are used to photograph the sun and the wedge.) With these plates a nearly clear background was obtained, and the results were very concordant.

To obtain thorough stirring and an even development, the plates were developed, four at a time, in a tank just half-filled with dilute developer, and the tank was constantly and rapidly reversed by hand throughout the development. To avoid some surface markings on the plates, the makers suggested soaking in water for five minutes before developing, and this proved a great advantage.

An important point arises owing to the different wave-length of the light used in photographing the sun and the standard wedge, since no constant

* 'Roy. Soc. Proc.,' A, August, 1920.

source of ultra-violet light is available. It is well known that the law of blackening is different for different wave-lengths, but for this method of

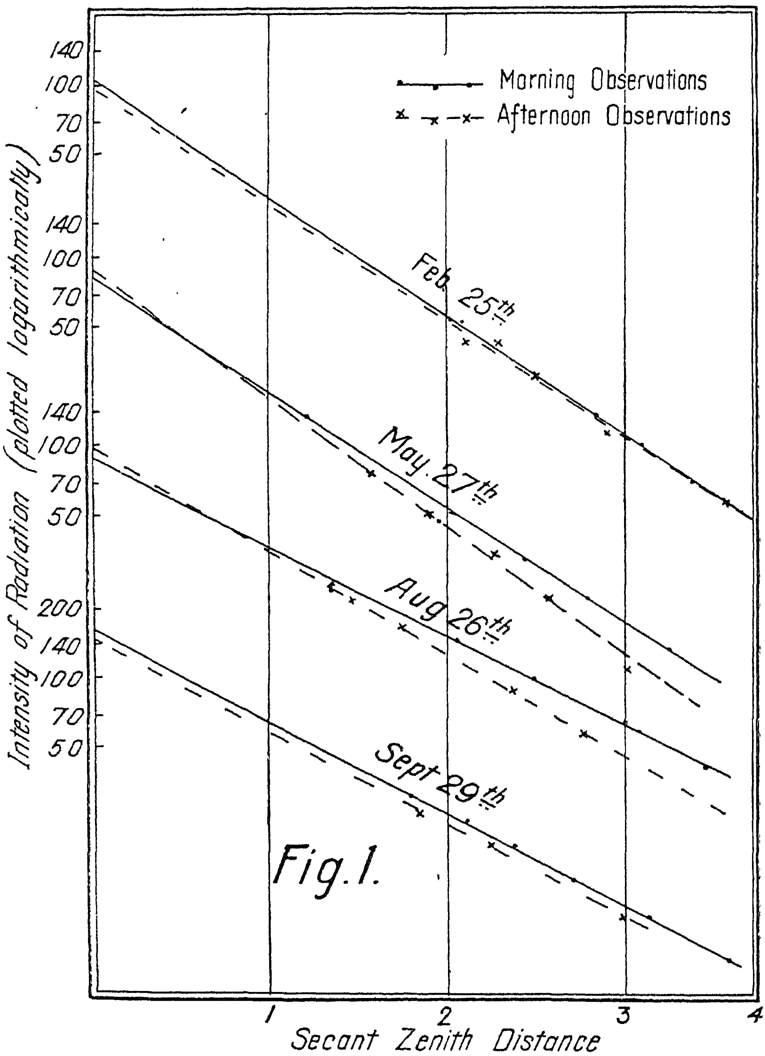


Fig. 1.

working it is not necessary to know the law, provided only that it is of the same form for the two wave-lengths used. The distance along the wedge which corresponds to a change of light of known ratio is found by taking two photographs of the sun on clear days near noon, with and without a rotating gauze in front of the object lens of the camera—the ratio of clear to total area of the gauze being known. It was found that the constant differed for the two wave-lengths by about 20 per cent.

When the precautions mentioned above are taken, it appears that the measurements of the intensity of the sunlight are very good, and troubles due to change in clearness of the atmosphere are probably much the most serious.

In a climate such as that of England, one cannot expect the transparency of the atmosphere always to remain constant during the three hours necessary for making one set of observations. One is liable to obtain erroneous results from this cause even though the instrumental methods of measuring the intensity of sunlight may be perfect.

An attempt was therefore made to find a method of measuring the transparency of the atmosphere by a single brief observation so that changes in transparency could be allowed for.

Over the range of wave-lengths in which we are interested, the reduction of energy in the direct solar beam, by the atmosphere, appears to be chiefly due to scattering.* Measurement of the variation in the amount of scattering will thus indicate the variation in the transparency. As the scattering increases, the brightness of the sky near the sun will increase greatly, and the brightness of the direct sunlight will decrease slightly. An instrument was, therefore, made to measure the relative amount of light from a small area of sky just round the sun and that direct from the sun. This ratio (R) will measure the scattering for the wave-length used.

Obviously the scattering will depend both on the length of the path traversed by the solar beam through the atmosphere, and on the amount of scattering material present. The relative length of path can be obtained from the sun's altitude, so that knowing the law connecting the variation of the ratio (R) with length of path, we obtain the amount of scattering material for a given length of path (say for vertical beam), and this should indicate the transparency of the atmosphere. The relative length of path is closely given by the secant of the sun's zenith distance (sec Z). It is not easy to calculate how (R) should vary with sec Z, but to a rough approximation it is obvious the R/sec Z should be constant if the transparency is fairly high.

It is surprising how much the transparency of the atmosphere varies from minute to minute at times when the sky appears almost uniformly clear. This is particularly so when clouds of the Fracto-Cumulus type are about. Even before any actual clouds appear or after they evaporate there seem to be masses of haze, barely visible to the eye, but which have considerable effect on the transparency.

* See Smithsonian 'Misc. Coll.,' vol. 69, No. 3.

5. *Results.*—The following table gives the actual values (in arbitrary units) obtained for the intensity outside the atmosphere of solar radiation of wave-length approximately $0{\cdot}32\mu$, and also the transmission coefficient of the atmosphere for radiation of this wave-length. (Fig. 3 shows the same results graphically.) The fifth column gives the character of the observation according to the nearness with which the individual observations lie on a straight line in the "log I—sec Z" plot. The last column gives the value of the solar constant as measured by the Smithsonian Institution for all cases where approximately simultaneous measurements were made.

Values of Solar Radiation and Atmospheric Transmission Coefficient.

Date.	Time.	I_0.	α.	Character.	Smithsonian Values of Solar Constant.
1922					cal/cm²/min
Feb. 18	p.m.	175	0·30	Good	1·952
,, 22	a.m.	46	0·285	Fair	1·958
,, 25	a.m.	104	0·31	Fair	1·936
,, 25	p.m.	96	0·32	Fair	1·936
,, 27	a.m.	104	0·31	Fair	—
,, 28	a.m.	66	0·385	Poor	1·940
Mar. 2	a.m.	74	0·36	Fair	1·944
,, 4	p.m.	233	0·24	Fair	1·939
,, 23	a.m.	123	0·28	Good	1·943
April 2	a.m.	112	0·28	Good	1·939
,, 5	a.m.	109	0·29	Poor	1·929
,, 13	a.m.	74	0·29	Good	—
,, 17	a.m.	96	0·295	Fair	1·924
,, 19	p.m.	136	0·25	Good	1·923
May 4	p.m.	74	0·28	Good	1·919
,, 5	p.m.	103	0·22	Fair	—
,, 13	a.m.	50	0·355	Poor	1·934
,, 14	p.m.	92	0·27	Excellent	1·923
,, 19	p.m.	65	0·31	Good	1·935
,, 21	p.m.	84	0·275	Good	1·938
,, 27	a.m.	83	0·34	Good	1·937
,, 27	p.m.	88	0·295	Good	1·937
,, 28	a.m.	100	0·24	Poor	1·897
,, 29	a.m.	71	0·25	Good	1·908
June 4	a.m.	100	0·255	Good	1·933
,, 5	a.m.	74	0·27	Good	1·929
,, 11	p.m.	88	0·215	Good	1·941
,, 16	a.m.	54	0·37	Poor	1·930
July 10	a.m.	44	0·43	Excellent	1·911
Aug. 20	p.m.	67	0·385	Poor	—
,, 26	a.m.	88	0·44	Excellent	1·915
,, 26	p.m.	99	0·38	Good	1·915
Sept. 10	a.m.	101	0·415	Good	1·905
,, 17	p.m.	200	0·34	Good	—
,, 18	a.m.	133	0·40	Good	1·866
,, 21	p.m.	182	0·31	Very poor	—
,, 29	a.m.	155	0·415	Good	—

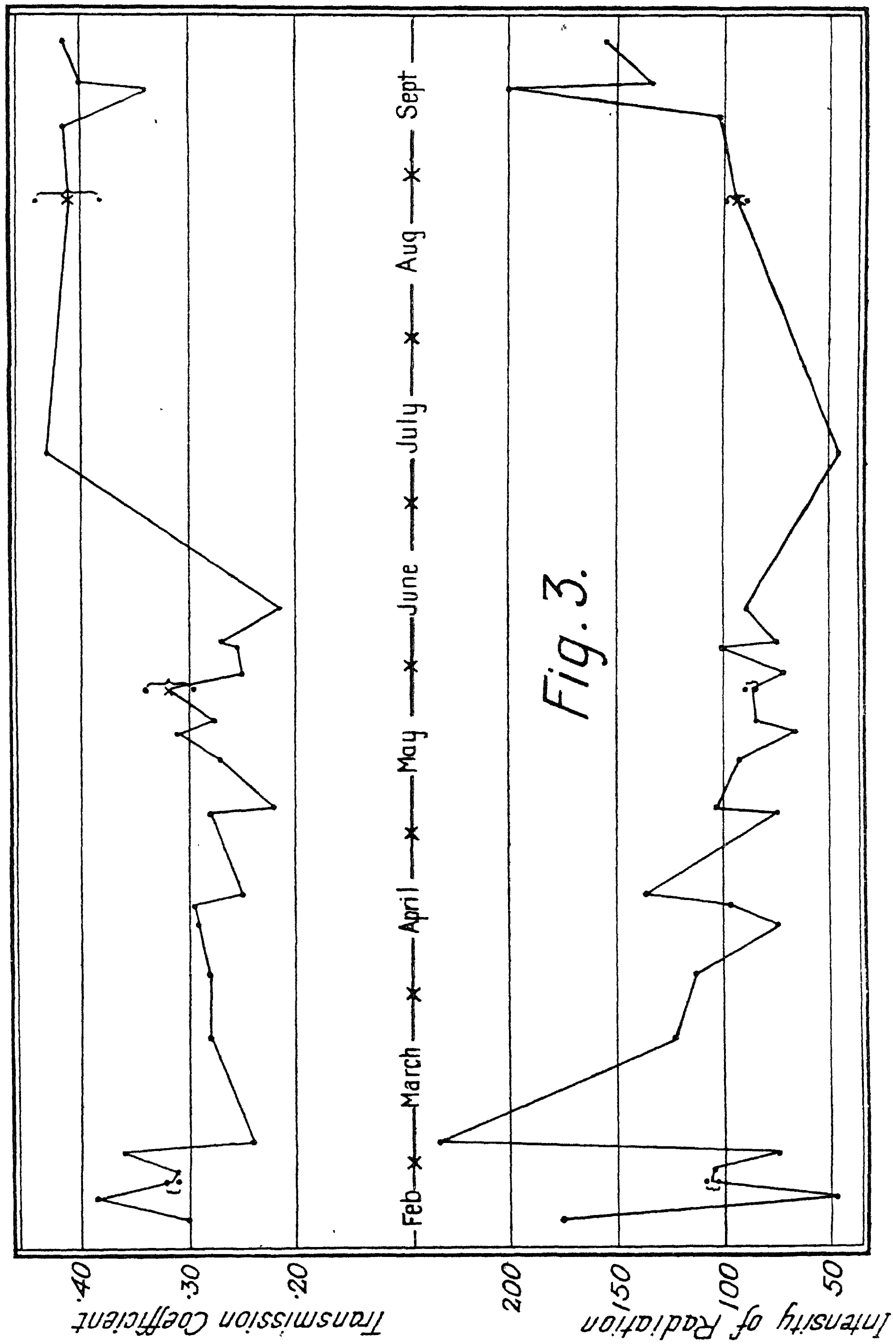


Fig. 3.
Feb
March
April
May
June
July
Aug
Sept
Transmission Coefficient
·40
·30
·20
Intensity of Radiation
200
150
100
50

Variations of Solar Radiation.—The variations from day to day in the intensity of radiation $\lambda = 0 \cdot 32 \mu$ appear to be surprisingly large. If we omit all days classed as "poor" the standard deviation of the remaining observations is 39 per cent. of the mean. This value is, however, largely influenced by two very high readings, and if we omit these a value of about 30 per cent. would be obtained. If the observations are further selected, and only "good" and "excellent" observations used, where the experimental error would most certainly appear to be small, a standard deviation of 35 per cent. is obtained. This result is again largely influenced by one very high value, and if this be omitted the standard deviation is again reduced to 30 per cent.

We may thus take the value of at least 30 per cent. of the mean as being the standard deviation of the measured variations in solar radiation of this wavelength. If we allowed a standard error of observation of 10 per cent. we should still be left with a real variation having a standard deviation of at least 28 per cent., while a standard error of 20 per cent. (which seems to be certainly excessive) would only reduce the standard deviation of the true variation to 22 per cent.

Dr. Abbot of the Smithsonian Institution has kindly forwarded advance figures of the Solar Constant on the days when ultra-violet measurements were made at Oxford. These are given in the last column of the previous table. If one omits two days in September, which do not agree at all, there appears to be a slight connection between the two sets of figures. It must, however, be noticed that the range of solar constant values (except on the two days in September) was very small, being only 2 per cent. of the mean. It is not surprising that the correlation is small, since it is quite likely that the chief cause of variations in the U.V. radiation is different from that for the total radiation (compare atmospheric transmission coefficients, page 262).

Contrast between the Centre and Limb of the Sun.—It is well known that the ratio of the apparent brightness of the centre and limb of the sun's disc is not constant from day to day, but varies by a small amount. Also both the average contrast, and the variations in contrast, are greater for short wavelengths than for long. Schwartzchild and Villager have measured the average contrast for the light which passes through a silver screen.* A few of the photographs taken in this work were therefore measured to determine the variations in contrast from day to day. It was found that the changes in contrast were very small—within about 5 per cent. of the mean value. The actual values are given in the following table.

* 'Astrophys. Journ.,' vol. 23, p. 284 (1906).

Variations in Contrast across the Sun's Disc.—Values of contrast are ratio of brightness $12\frac{1}{2}$ per cent. and $87\frac{1}{2}$ per cent. of the sun's radius from the centre :—

Date. 1922.	Contrast. Per cent.
February 18	50
,, 22	$56\frac{1}{2}$
,, 25 (a.m.)	$54\frac{1}{2}$
,, 25 (p.m.)	$52\frac{1}{2}$
,, 27	$54\frac{1}{2}$
,, 28	$52\frac{1}{2}$
March 2	52
,, 4	54
,, 23	53
April 2	50
,, 13	55
,, 17	$50\frac{1}{2}$
,, 19	52

Average contrast 52·8 per cent.

It is of interest to note that the average value formed by Schwartzchild and Villager for the same positions along the radius is 53·3 per cent., which is in very good agreement with the results found here.

In the case of the contrast in total radiation, it has been shown by the Smithsonian Institution that there is a connection between contrast and total radiation. The connection, however, is very small and would not be expected to be shown in the small number of observations used here, and this is found to be the case.

Connection between the Sun's U.V. Radiation and other Solar Phenomena.—I am indebted to Professor H. H. Turner for supplying me with figures of the areas of H_α markings on the sun's disc, as measured at Kodaikanal and Mt. Wilson, and to the Astronomer Royal for areas of sun-spots, for the days on which the sun's ultra-violet radiation was measured at Oxford.

The connection between H_α markings and the ultra-violet radiation is not definite, but a large ultra-violet radiation seems on the whole to go with small area of H_α markings.

Since 1922 is near a sun-spot minimum, the areas of sun-spots on all days when ultra-violet radiation was measured are very small except for three days about the beginning of March. For this reason it is impossible to tell whether or not there would be any connection between sun-spots and ultra-violet radiation.

It would seem that the larger changes in the sun's ultra-violet radiation must be due to changes in the scattering and absorbing power of the layers of gas in or above the photosphere. It is possible that the material of the corona may have some effect, but the amount of material is so small that the effect is probably not great.

Transmission Coefficient of the Earth's Atmosphere (α).—The transmission coefficient of the atmosphere (*i.e.* the ratio of incident to transmitted radiation for vertical rays) varies very greatly from day to day for light of this short wave-length. If we omit observations classed as "poor" there appears to be only a small connection between α and intensity of emitted U.V. radiation. This is so far satisfactory, since it shows that any error in the value of the emitted radiation due to changes in transparency of the atmosphere during the observations is small.

There appears to be a small decrease in the transparency of the atmosphere through the day, since the mean transmission coefficient for the morning observations is some 10 per cent. higher than that for the afternoon observations.

An interesting point arises when we compare the haziness of the atmosphere with the transmission coefficient for $\lambda = 0\cdot32\mu$. One would naturally assume that hazy days would have small transmission coefficients, and indeed, on very hazy days, no observations were made, as it was thought that they would be valueless. When each photograph was taken, the state of the sky was noted and recorded as "clear," "hazy," etc. If now we separate the observations according to the apparent state of the sky at the time (omitting observations classed as "poor") we obtain the following mean values for the transmission coefficients.

Transmission Coefficients and Haziness.—

State of Sky.	Transmission Coefficient.
"Very clear"	0·27
"Clear"	0·28
"Rather hazy or whitish"	0·325
"Hazy"	0·26

It thus appears that there is no connection whatever between the estimated haziness of the atmosphere and the transmision coefficient for $\lambda = 0\cdot32\mu$.

During the summer, the instrument for measuring the haziness was constructed, and its readings at the time each photograph was taken are available for the latter part of the summer. Here again there appears to be no connection between the amount of "haze" and the transmission coefficient for $\lambda = 0\cdot32\mu$,

the correlation between them being $+0 \cdot 15$. (The positive sign would indicate an increased transmission coefficient with increased haziness.)

These results indicate that the cause of variations in the ordinary "haziness" of the atmosphere is different from that causing variation in transparency for $\lambda = 0 \cdot 32\mu$.

It has been shown by the Smithsonian Institution that scattering of light in the atmosphere is mainly due to three causes, viz.: (i) "large" dust particles, which scatter all wave-length alike; (ii) "small" particles, the number of which seems to be associated with the amount of water vapour in the atmosphere and will scatter different wave-length according to the λ^{-4} law; (iii) air molecules which also scatter according to the λ^{-4} law.

It is, therefore, natural to suggest that the "large" particles are chiefly responsible for changes in "ordinary haziness," and this is almost certainly true; and that the effect of "small" particles, while negligible for long wave-lengths, is predominant for short wave-lengths. Now the transmission coefficients for various wave-lengths in the visible region have been measured on a great many days by the Smithsonian Institution, and if we plot log α against λ^{-4} we can determine at once how much of the changes from day to day are due to "large" particles and how much due to "small" ones. Thus it appears that for Washington, variations of the "large" particles may change α from about $0 \cdot 78$ to about $0 \cdot 90$, or over a range of 14 per cent. of the mean value. Such a change in the number of "large" particles would, of course, also cause a change in the transmission coefficient for $\lambda = 0 \cdot 32\mu$ over a range of 14 per cent., *i.e.* we might expect values to range from $0 \cdot 28$ to $0 \cdot 32$ from this cause. Since the actual values range from about $0 \cdot 22$ to $0 \cdot 44$, such a small change as that produced by the "large" particle at Washington might be quite masked by other causes.

The instrument and light filter used here for measuring "haze" will indicate the scattering of light of approximately $\lambda = 0 \cdot 6\mu$. If we take the transmission coefficient for $\lambda = 0 \cdot 6\mu$ as $0 \cdot 75$, which is the mean value at Washington, then the maximum and minimum values recorded here by the haze instrument would indicate variations in α for $\lambda = 0 \cdot 6\mu$ from $0 \cdot 66$ to $0 \cdot 87$, which agrees fairly well with the actual variations found at Washington.

Further a change in the scattering by "small" particles corresponding to a change in transmission coefficient (α) for $\lambda = 0 \cdot 32\mu$ from $0 \cdot 25$ to $0 \cdot 44$ would only change the transmission coefficient for $\lambda = 0 \cdot 6\mu$ by less than 5 per cent., which might easily be masked by the much larger changes due to "large" particles.

Thus the assumption that the variations in transparency for $\lambda = 0\cdot6\mu$ are chiefly due to "large" particles and that for $\lambda = 0\cdot32\mu$ to "small" particles seems quite satisfactory. If this is so, the "large" and "small" particles must vary quite independently of each other.

Amount of Ozone in the Atmosphere.—Until recently, the only measurements of the proportion of ozone in the atmosphere were those made by chemical means. The most thorough study seems to have been made by Pring,* who, by sending up a small apparatus on free balloons, found the average proportion of ozone in the air between the ground and about 15 km. These measurements indicated a concentration of ozone of about 2×10^{-6}. If this result were correct, the absorption of radiation at $\lambda = 0\cdot32\mu$ by ozone would be quite appreciable. For this reason, experiments were begun to measure the transmission coefficient both for $\lambda = 0\cdot32\mu$ and for longer wave-lengths, in order to estimate the concentration of ozone each day.

When this apparatus was just completed, a paper by Fabry and Buisson† was published, in which the concentration of ozone, measured by spectroscopic methods, is given. These measurements indicate a concentration of ozone nearly ten times smaller than those of Pring, and if correct would lead to an absorption of ozone by radiation of $\lambda = 0\cdot32\mu$, which is small compared with that due to scattering. That the amount of ozone given by Fabry and Buisson is approximately correct is shown by plotting the logarithm of the transmission coefficients for various wave-lengths, as found at Washington, against λ^{-4}. By extrapolating we may find the transmission coefficient due to scattering for other wave-lengths. Now while the points for Washington, which are given down to $\lambda = 0\cdot39\mu$, do not lie well on a straight line, they would indicate that the average transmission coefficient for $\lambda = 0\cdot32\mu$ due to scattering alone is certainly not greater than $0\cdot3$. It will be seen that this agrees closely with the result obtained here by actual measurement, so that the effect of absorption by ozone must be small and therefore the concentration must be less than that given by Pring. If Fabry and Buisson's values are correct, absorption by ozone will be unimportant for wave-lengths greater than about $0\cdot30\mu$. It would be very simple to measure the amount of ozone in the atmosphere if only a suitable light filter could be found, *i.e.* one transmitting a narrow band in the ultra-violet (as in the case of silver) for a wave-length of about $0\cdot30\mu$. All that appears to be necessary is to construct a photo-

* 'Roy. Soc. Proc.,' A, vol. 90 (1914).

† 'Astrophys. Journ.,' December, 1921.

graphic haze-measuring instrument, similar to the one already described, and to add filters for $\lambda = 0 \cdot 32\mu$ and $\lambda = 0 \cdot 30\mu$.

6. *Sources of Error and Checks on the Accuracy of Measurements.*—The possible sources of error may be divided into two distinct classes: (1) Instrumental, *i.e.* errors in the actual measurement of the radiation reaching the earth's surface; (2) Atmospheric, *i.e.* changes in transparency of the atmosphere during the time occupied in obtaining the series of observations necessary each day.

(1) Instrumental Errors.—The plots of four days (logarithm of intensity against secant of zenith distance) are shown in fig. 1. These are quite typical plots, and show the nearness with which the observed values lie on a straight line. If we take such a set as the morning of August 26 or September 29, it is seen that the agreement with a straight line is very close, and the other sets are as good or better than these. If there were any considerable instrumental error, such results could hardly be obtained, since it is extremely improbable that instrumental errors should just compensate for errors due to atmospheric changes. (It may be noted that when measuring the images with the photo-electric apparatus, the galvanometer and wedge settings can easily be obtained with an error of less than 1 per cent.)

There is a known systematic error due to the fact that the centre of an image on a photographic plate tends to be under-developed, either because fresh developer cannot diffuse through the gelatine sufficiently fast, or more likely because the products of development cannot diffuse out quick enough and retard the development. That it is not due to defective stirring is shown by the fact that increased stirring does not appreciably reduce the error. This error, however, is not large, and in any case is systematic, so that it will not affect the magnitude of the variations from day to day.

Finally, it is shown later that the contrast in brightness between the centre and limb of the sun is nearly constant, which could not be the case if there were serious errors, besides which the very close agreement with the average contrast found by Schwartzchild and Villager is again entirely satisfactory.

(2) Much more serious is the second class of errors, viz., those due to changes in atmospheric transparency during the observations. Another year it is hoped to use an instrument similar to the haze-measuring instrument already described, but working with light of the same wave-length as that of the main observations, viz., $0 \cdot 32\mu$. Without this, however, there is no means of eliminating this source of error. All one can do is to class the days as "poor,"

"fair," "good," etc., according to the nearness with which the observations lie on a straight line. This, however, should be a fairly good guide, since a uniformly changing transparency would lead to points lying on a curve rather than a straight line. Unfortunately there were only four days when both morning and afternoon observations could be made, but the agreement in the value of the intensity for sec $Z = 0$ in these morning or afternoon observations made the same day is quite good, as will be seen from fig. 1. The percentage differences are respectively 8, 6, 12 and 7 per cent., and it must be remembered that a certain real variation must be expected in the eight hours or so which elapse between morning and afternoon observations.

On the whole it seems likely that the standard error of observation may be somewhere about 10 per cent., and it is almost certainly less than 20 per cent. if observations classed as "poor" are omitted.

An entirely independent proof that the observed variations in the sun's radiation at $\lambda = 0{\cdot}32\mu$ are real, and not due to changes in transparency of the atmosphere during the observations, may be obtained as follows.

Consider the plot, fig. 2, showing the relation between the observed intensity

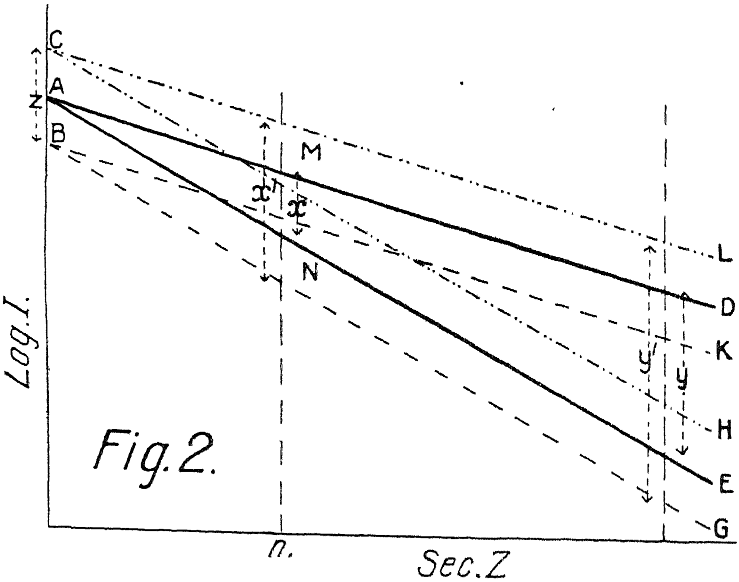


Fig. 2.

of radiation at the earth's surface (I') and sec Z. Suppose the actual radiation outside the atmosphere (I_0) to be constant, and let A on the plot represent its true value (say equal to the mean observed value). Let AD and AE be lines on the plot representing the maximum and minimum transparency of

the atmosphere, and let n_1 and n_2 be two values of sec Z at which observations have been made. Now apart from instrumental errors, all values of log I′ for sec $Z = n_1$ must lie between M and N on the plot, *i.e.* within a range $= x$. Similarly, the range of values of log I′ for sec $Z = n_2$ must lie within a range y, and $x/y = n_1/n_2$.

Thus, if there is no real change in solar radiation emitted, we should find the average deviations of the observed value of log I′ according to the above equation.

Suppose now that there is a real variation of log I_0 equal to z in the plot, then if B and C represent the maximum and minimum values and CL, BK, CH and BG, the lines corresponding to maximum and minimum transparency of the atmosphere, the observed values of log I′ will now have ranges of x' and y', and $x'/y' = (x+z)/(y+z)$.

Thus the ratio of the average deviations of log I′ for sec $Z = n_1$ and sec $Z = n_2$ will be greater than that found in the first case.

The observed average deviations of I′ have been found for sec $Z = 1 \cdot 5$ and sec $Z = 3 \cdot 5$ for two groups of observations. (Owing to a large semi-permanent change in the average value of α about the middle of June it is desirable to keep observations before and after this date separate). Omitting "poor" results as usual we find the following ratios of the average deviations.

Ratio of Average Deviations of Log I′ at sec $Z = 1 \cdot 5$ and sec $Z = 3 \cdot 5$.

Group.	n_1/n_2.	x'/y'.	Number of Observations.
February 18 to June 11	0·43	0·66	23
July 10 to September 29	0·43	1·10	7

Thus, there is no doubt that x'/y' is much greater than n_1/n_2 showing that the changes in I_0 are real and not due to atmospheric changes.

7. *Connection between Observed Variations and Terrestrial Weather, etc.*—One would not expect variations in local weather in temperate regions to be directly affected by variations in solar radiation, but only average condition over a wide area of the earth, or values for equatorial stations. It is unfortunate that a considerable time must elapse before these observations are available so that at present we have no suitable material with which to compare the

solar variation. Moreover, the small number of observations obtained in 1922 makes it desirable to obtain more observations another summer before attempting seriously to decide whether or not there are such connections. On the other hand, variations in the transparency of the atmosphere would be expected to vary with local conditions.

A most marked increase in the transparency of the atmosphere for this radiation occurred about June of 1922, the average value of α rising from about 0·27 to about 0·42. Moreover, it should be noted that the fine weather of the spring and early summer suddenly broke down about the middle of June, the latter part of the summer being very unsettled and wet. That this change is not due to any instrumental defect is shown by the fact that the values of the solar contrast and of I_0 remained much as before.

The most obvious explanation would be that the "dust" was washed out of the atmosphere by the wet weather, with resulting increase in α. But, on the other hand, much cyclonic or wet weather was experienced in February and March,* when low values of α were found. It appears probable that the increase in α was due to a diminution of the "small" particles in the atmosphere, but why these decreased and whether they affected, or were affected by, the change of weather cannot be settled at present.

As regards the connection of α with local conditions the results are not very regular, and in any case the number of observations is too small to warrant definite conclusions, especially as it seems desirable to treat observations after June separately. So far as these observations go, however, high values of α seem to be associated with (1) low pressure ; (2) rising barometer ; (3) disturbed cyclonic conditions ; (4) south-westerly winds ; while low values of α seem to be associated with (1) high pressure ; (2) falling barometer ; (3) anticyclonic conditions (especially the edge of an anticyclone) ; (4) north and north-easterly winds. The results are not sufficiently regular, however, to say that these are not accidental effects.

The writer is greatly indebted to Prof. Lindemann for many valuable suggestions during the progress of the work.

Appendix.

8. *Short Methods of Measuring Atmospheric Transmission Coefficient.*—The measurement of the absolute intensity of radiation received from the sun

* Moderately high values of α were found prior to March 4, but the cyclonic weather continued until April. It may be noted that the beginning of March was a period of great sunspot activity.

outside the earth's atmosphere necessarily involves two steps: (i) measurement of the absolute intensity of radiation received at the earth's surface for a given sun's altitude; (ii) measurement of the atmospheric transmission coefficient for various wave-lengths. The latter value is usually obtained by measuring the relative radiation received at the earth's surface for various altitudes of the sun. This is a lengthy and laborious process, and also possesses the disadvantage that any change in transparency during the observations will lead to erroneous results.

For these reasons a short method has been introduced by the observers of the Smithsonian Astrophysical Department, which is somewhat analogous to the method of measuring haze described above. In the new Smithsonian method the amount of energy of all wave-lengths received from an area of sky, 20 degrees round the sun—but excluding the sun—is measured when the sun is at a fixed altitude; let this be P. The amount of water vapour in the atmosphere is found from the intensity of the water-vapour bands—let ρ be the energy received at the centre of the band and ρ' that which would be received if no water were present—as estimated from the energies received on either side of the band—then ρ'/ρ is a function of the amount of water in the atmosphere. Let $P\rho'/\rho = F$, and the transmission coefficient for any wave-length λ be α_λ. Now it is found that if the values of α_λ (as found by the usual method) are plotted against F, the points are grouped roughly about a smooth curve (though they are very far from lying exactly on the curve). Once these curves have been obtained, the value of α_λ for any day is obtained from the value of F, which is comparatively easily measured.

This method is admittedly almost entirely empirical, and from the diagrams given* it would appear that it is only made possible by the very clear air at observing stations. One weak point seems to be that the values of α_λ for all the different wave-lengths are obtained from one observation on white light, while it is not necessary that the transparencies for light of all wave-lengths should vary alike from day to day.

The principle of the haze-measuring instrument described above suggests an obvious improvement, one form of which would be as follows:—The two patches of light from the sun, and the sky close to the sun, respectively, are allowed to fall on the slit of a spectrograph, and the relative intensities of sky and sunlight for each wave-length are measured (say by one of the methods used above). The ratio of intensities being a function of the scattering of light of the wave-length used and sun's altitude, it can be employed to obtain the transmission

* Smithsonian Inst., 'Astrophys. Obs. Annals,' vol. iv, p. 82.

coefficient for that wave-length (in all those parts of the spectrum where there is little absorption). What may be termed the "calibration" of the instrument must, of course, be made with the aid of the usual long-method measurements of α_λ, *i.e.* employing observations at various sun's altitudes. It is hoped to test this method in practice during the coming summer.

It is of interest to note that so long as the transmission coefficient is high there is no need to measure the haze accurately. For if R be the ratio of skylight to sunlight, and H the effective amount of scattering material in the atmosphere which scatters light of the wave-length used, we may put the variation of R with sec Z,

$$H_\lambda = C_\lambda R_\lambda / \phi (\sec z).$$

Also the effect of the haze on α may be put

$$\alpha_\lambda = e^{-k_\lambda H_\lambda};$$

or

$$\alpha_\lambda = e^{-k_\lambda C_\lambda R_\lambda \cdot \phi (\sec z)},$$

and

$$\frac{d\alpha_\lambda}{\alpha_\lambda} = -k_\lambda C_\lambda R_\lambda / \phi (\sec z) \times \frac{dR_\lambda}{R_\lambda}$$

$$= \log_e \alpha \times \frac{dR_\lambda}{R_\lambda}.$$

Thus so long as $\log_e \alpha$ is small, R need not be measured very accurately. On clear days at Calama (Chile), α lies between 0·70 and 0·95 for the visible light.

Summary.

Measurements have been made of the ultra-violet radiation of wave-length $0 \cdot 32\mu$, which is emitted by the sun, on 34 days in 1922.

The percentage variation of the radiation from day to day is large, having a standard deviation of about 30 per cent., which is much greater than might be expected from a consideration of the variations of the "solar constant."

The atmospheric transmission coefficient for this radiation is also found, and appears to vary from about 0·22 to about 0·42. It is shown that the errors of observation cannot be very large.

The contrast in brightness between the centre and limb of the sun was measured for a wave-length of $0 \cdot 32\mu$ but found to vary less than $\pm$ 5 per cent. from day to day.

The reduction of this radiation in passing through the atmosphere is shown to be chiefly due to scattering by particles which are small enough to scatter according to the inverse fourth power of the wave-length. The large variations

in transparency which occur from day to day are not closely related to the ordinary "haziness" of the atmosphere, which is probably due to much larger particles. A large increase in transparency (for $\lambda = 0 \cdot 32 \mu$) occurred about June, 1922, which may be connected with the marked change in the general weather which took place about the same time.

An instrument for measuring the amount of scattering of light of any wave-length from the direct solar beam has been made, and a method of measuring the solar constant by one brief observation is outlined.

On Seismic Waves in a Visco-Elastic Earth.

By NINA M. HOSALI, B.Sc., University College, London.

(Communicated by Prof. L. N. G. Filon, F.R.S. Received May 14, 1923.)

§ 1. *Stress and Strain in a Visco-Elastic Medium.*

Experiments have shown that the rocks which form the outermost crust of the Earth differ in their behaviour under stress from that of an ideal elastic solid, one of the more important departures being the possession of "viscous" properties.

Galitzin, Nagaoka and Rudski have proposed to take account of viscosity by adding a "frictional" term or terms to the equations of motion of the ordinary theory of elasticity, and have applied the modified equations to problems of seismology.* An alternative procedure is to assume some stress-strain-time law, and from this to deduce the laws of wave-propagation.

Prof. L. N. G. Filon has suggested that the stresses in a visco-elastic medium might be regarded as derived from the addition of ordinary elastic solid stresses, and stresses in a viscous fluid. If u, v, w be the component displacements, and δ the dilatation, the formulæ for the normal tractions are three of the type

$$\widehat{xx} = \{-\Pi + \sigma\, \partial\delta/\partial t + 2\nu\, \partial/\partial t\, (\partial u/\partial x)\} + \lambda\delta + 2\mu\, \partial u/\partial x, \qquad (1)$$

where λ, μ are Lamé's elastic constants, ν is the coefficient of viscosity, Π the

* Galitzin, 'Bull. de l'Acad. des Sc., St. Péts.,' Sér. 6, p. 219 (1912); Nagaoka, 'Proc. Tokyo Math.-Phys. Soc.,' vol. III, p. 17 (1906); Rudski, 'Bull. Intl. de l'Acad. des Sc. de Cracovie' (1898), or 'Beitr. z. Geoph.,' vol. 4, p. 47 (1900).

so-called "hydrostatic pressure" in the viscous fluid, and σ is a constant. If we choose σ so that $\sigma = -(2/3)\,\nu$, we have

$$\tfrac{1}{3}(\widehat{xx} + \widehat{yy} + \widehat{zz}) = -\Pi + (\lambda + 2\mu/3)\,\delta = -\mathrm{P}, \text{ say.}$$

We now make the assumption that $\mathrm{P} = -\kappa\delta$, where κ is a constant; that is, we assume that the medium has a definite modulus of compressibility, κ, or in other words, that the hydrostatic pressure (Π) is proportional to the cubical compression. We then have

$$\widehat{xx} = \kappa\delta + 2\,(\mu + \nu\,\partial/\partial t)\,(\partial u/\partial x - \tfrac{1}{3}\delta), \text{ etc., etc.,} \tag{2}$$

while the expressions for the shears are

$$\widehat{yz} = (\mu + \nu\,\partial/\partial t)\,(\partial w/\partial y + \partial v/\partial z), \text{ etc., etc.} \qquad (3)^*$$

§2. *Comparison of Stress-Strain Laws with Observation.*

Whatever may be the grounds on which a theory relating stress and strain in a visco-elastic body is based, its value from the seismological point of view will largely depend on the closeness with which it represents the actual behaviour of known substances, and especially of typical rocks, under some simple form of stress, *e.g.*, tension.

If S be the longitudinal stretch under a total tension F, we find from (2) and (3),

$$\mathrm{S} = \mathrm{F}/9\kappa + (1/3\nu)\,e^{-\mu t/\nu}\int_0^t \mathrm{F}e^{\mu t/\nu}\,.\,dt \qquad (4)\dagger$$

The first term implies an immediate strain proportional to the load. The latter being applied suddenly and maintained at a constant value, the strain, after the initial stretch on loading, follows an exponential law and attains its final value asymptotically.

Several other stress-strain-time laws have been discussed by Dr. H. Jeffreys, and one of them—due to Sir Joseph Larmor—has been applied by him to the case of spherical distortional earthquake waves, the viscosity being assumed small.‡

* Similar expressions for the stresses have been given by P. Duhem ("Recherches sur l'Elasticité," part II, chap. I, § 4). In Duhem's formulæ for the tractions, however, the quantity π is replaced by a constant, and no relation is assumed between the constants ν and σ.

† See L. N. G. Filon and H. T. Jessop, "On the Stress-Optical Effect in Transparent Solids strained beyond the Elastic Limit," 'Phil. Trans. Roy. Soc.' (A), vol. 223, p. 95 (1922).

‡ 'Roy. Astron. Soc. Notices,' vol. 77, p. 449 *et seq.* (1917).

The law in question may be written

$$S = (1/n\tau)\, e^{-t/\tau} \int_0^t F e^{t/\tau} \, . \, dt. \tag{5}$$

According to this law there is no instantaneous strain; under a constant load the strain increases gradually from zero, attaining its final value exponentially after an infinite time.

Now the experiments of Filon and Jessop (*loc. cit.*) on celluloid under tension, of Andrade* on metals under tension, of Adams and Coker on rock specimens under compression,† and of Nagaoka‡ and Kusakabe§ on rocks under bending and torsion, have shown that an instantaneous strain is a fundamental phenomenon displayed by a wide range of substances. After the initial yield, the strain increases at first rapidly, but afterwards (provided the load be not excessive) at a small or negligible rate. The law expressed by equation (4) is thus in rough qualitative agreement with the behaviour of known substances under stress, and appears to give a better representation of experimental results than other stress-strain laws which have been suggested. It has, therefore, been thought worth while to apply the theory from which it is derived to the subject of seismic wave propagation.

§ 3. *Plane Waves in a Visco-Elastic Medium.*

The equations of motion are obtained by inserting expressions (2) and (3) for the stresses in the equations

$$\partial\,(\widehat{xx})/\partial x + \partial\,(\widehat{xy})/\partial y + \partial\,(\widehat{xz})/\partial z = \rho\, \partial^2 u/\partial t^2, \text{ etc., etc.,}$$

and are three of the type

$$\{\kappa + \tfrac{1}{3}(\mu + \nu\,\partial/\partial t)\}\,\partial\delta/\partial x + (\mu + \nu\,\partial/\partial t)\,\nabla^2 u = \rho\,\partial^2 u/\partial t^2. \tag{6}$$

If the motion is simple harmonic, so that the displacements are proportional to e^{ipt}, say, the expressions for the stresses and the equations of motion take precisely the same forms as the corresponding equations of ordinary elastic theory, the constants λ and μ being, however, replaced by "complex elastic constants," λ' and μ', where

$$\lambda' = \kappa - \tfrac{2}{3}(\mu + ip\nu), \qquad \mu' = \mu + ip\nu. \tag{7}$$

Any solution of the ordinary equations of motion representing simple harmonic

* 'Roy. Soc. Proc.' (A), vol. 84 (1910); vol. 90 (1914).

† 'Carnegie Instn. of Washington Publns.,' No. 46, 1906.

‡ 'Phil. Mag.,' vol. 50, p. 58 (1900).

§ 'Journ. Coll. Sc. Japan,' vol. 20, Art. 9, p. 15, etc. (1905).

oscillations of an elastic body can, therefore, be utilised to solve a problem in the visco-elastic case, and it is only necessary to write λ' and μ' for λ and μ and then interpret the result. Relations between the stresses, leading to equations in u, v, w will also retain their form unchanged.

Solutions representing periodic plane damped waves travelling in the direction of x, say, are obtainable in the form

$$\delta = \mathrm{A}e^{-q_1 t}e^{i\xi(\mathrm{V}_1 t - x)}; \qquad \Omega = \mathrm{B}e^{-q_2 t}e^{i\xi(\mathrm{V}_2 t - x)}, \tag{8}$$

where Ω is the rotation, A and B are arbitrary constants, $\xi = 2\pi/l$, where l is the wave-length, and

$$\left.\begin{aligned} \mathrm{V}_1 &= \pm\sqrt{a^2 - (4\pi\nu'/3l)^2}, & \mathrm{V}_2 &= \pm\sqrt{b^2 - (\pi\nu'/l)^2}, \\ q_1 &= 8\pi^2\nu'/3l^2, & q_2 &= 2\pi^2\nu'/l^2. \end{aligned}\right\} \tag{9}$$

In these expressions a and b are the velocities of propagation of dilatational and distortional waves, respectively, in an elastic medium of constants κ, μ, ρ, and ν' is the "kinematic viscosity," ν/ρ. It is evident that viscosity reduces the velocity of propagation and renders it dependent on the wave-length; further, for each type of wave there exists a minimum wave-length such that waves of shorter length cannot be propagated at all.

In the case of a semi-infinite medium, a corresponding solution can be found, representing plane waves in which the disturbance is chiefly confined to the free surface, such waves being analogous to "Rayleigh Waves."* If the medium lie on the negative side of the plane $y = 0$, the solution may be assumed to be of the form

$$(u, v) = (\mathrm{Y}, \mathrm{Y}')\, e^{ip(t - x/c')}, \tag{10}$$

where Y, Y′ are functions of y only. The equation to determine c' is

$$\chi^3 - 8\chi^2 + 24\chi - 16 - 16\,\{\mu'/(\lambda' + 2\mu')\}\,(\chi^2 - 1) = 0, \tag{11}$$

where $\chi = c'^2\rho/\mu'$. Assuming the displacements to be of the same type as those in (8), namely,

$$u, v \propto e^{-q_3 t}e^{i\xi(\mathrm{V}_3 t - x)}, \tag{12}$$

so that

$$p = \xi\mathrm{V}_3 + iq_3 = \xi c', \tag{13}$$

we have

$$\chi = c'^2/(b^2 + i\xi\nu' c'), \tag{14}$$

and the equation in c' is of the seventh degree. The simplest case is that in which the medium is incompressible, so that $\kappa = \infty$. This makes λ' infinite

* Lord Rayleigh, "On Waves propagated along the Plane Surface of an Elastic Solid," 'Proc. Lond. Math. Soc.,' vol. 17 (1887).

and the solution is identical analytically with that for an elastic incompressible solid, c' being given by

$$c'^2 = \eta b^2 + i\eta\xi\nu' c', \tag{15}$$

where η is the real root of the cubic

$$\chi^3 - 8\chi^2 + 24\chi - 16 = 0. \tag{16}$$

The value of η (using a slight correction made by Bromwich to Lord Rayleigh's value) is $0 \cdot 91262$, and this gives

$$q_3 = (0 \cdot 9126)\, 2\pi^2\nu'/l^2, \qquad \mathrm{V}_3 = \pm 0 \cdot 9553\sqrt{b^2 - 0 \cdot 9126\pi^2\nu'^2/l^2}. \tag{17}$$

The complete expressions for the displacements are

$$\left.\begin{aligned} u &= i\mathrm{C}\left\{- e^{2(\pi/l)y} + 0 \cdot 5437 e^{(0 \cdot 5912\pi/l)y}\right\} e^{-q_3 t} e^{i\xi(\mathrm{V}_3 t - x)} \\ v &= \mathrm{C}\left\{e^{(2\pi/l)y} - 1 \cdot 839 e^{(0 \cdot 5912\pi/l)y}\right\} e^{-q_3 t} e^{i\xi(\mathrm{V}_3 t - x)} \end{aligned}\right\}, \tag{18}$$

where C is an arbitrary constant.

It appears from these expressions that the sole effects of viscosity are damping and dispersion; the vibrating particles move in elliptic orbits of the same eccentricity as those in ordinary Rayleigh waves. As for dilatational and distortional waves there is a minimum wave-length below which oscillatory motion is impossible.

Since the periods of seismic waves are given directly by the seismograph it is convenient to consider the damping and velocity as dependent on the period (τ) rather than on the wave-length. We then find for

$$\begin{matrix} \textit{dilatational} \\ \textit{waves} \end{matrix}\left\{\begin{aligned} \mathrm{V}_1 &= (a/\sqrt{2})\left\{1 \pm \sqrt{1 - (8\pi\nu'/3a^2\tau)^2}\right\}^{\frac{1}{2}} \\ q_1 &= (3a^2/4\nu')\left\{1 \mp \sqrt{1 - (8\pi\nu'/3a^2\tau)^2}\right\} \end{aligned}\right\} \tag{19}$$

$$\begin{matrix} \textit{distortional} \\ \textit{waves} \end{matrix}\left\{\begin{aligned} \mathrm{V}_2 &= (b/\sqrt{2})\left\{1 \pm \sqrt{1 - (2\pi\nu'/b^2\tau)^2}\right\}^{\frac{1}{2}} \\ q_2 &= (b^2/\nu')\left\{1 \mp \sqrt{1 - (2\pi\nu'/b^2\tau)^2}\right\} \end{aligned}\right\} \tag{20}$$

$$\begin{matrix} \textit{surface} \\ \textit{waves} \end{matrix}\left\{\begin{aligned} \mathrm{V}_3 &= (0 \cdot 9553 b/\sqrt{2})\left\{1 \pm \sqrt{1 - (2\pi\nu'/b^2\tau)^2}\right\}^{\frac{1}{2}} \\ q_3 &= (b^2/\nu')\left\{1 \mp \sqrt{1 - (2\pi\nu'/b^2\tau)^2}\right\} \end{aligned}\right\} \tag{21}$$

Since the positive sign in the velocity corresponds to the negative sign in the damping coefficient, and *vice versa*, it follows that for any given period there are two possible velocities of propagation. The more slowly travelling wave, however, will in general be enormously damped compared with the other, and so will be of lesser relative importance. We may, therefore, divide the whole range of possible waves into a lightly damped (quick travelling) series, and a heavily damped (slow travelling) series. For each type of wave there exists a minimum period such that waves of lesser period cannot be propagated at all.

The damping factors for the three kinds of waves are readily compared by considering the variation of the function

$$y = z\{1 \pm \sqrt{1-(2\pi\nu'/z\tau)^2}\}.$$

We find that dy/dz is positive or negative according as the radical is positive or negative. Hence, for the lightly damped waves $q_1 < q_2$ provided that $3a^2/4 > b^2$. In the case of the Earth this inequality will in general be satisfied, since a is approximately $1\cdot 8b$ for the outer quarter of the Earth's radius, and the ratio increases at greater depths (see Knott, 'Roy. Soc. Edin. Proc.,' vol. 39, p. 177 (1919)). A dilatational wave therefore suffers less damping than a distortional wave of equal period. In the heavily damped range the damping *increases* as the viscosity *decreases*; these waves are therefore only of importance when the viscosity is large.

§ 4. *Approximate Solutions for a Medium of Small Viscosity.*

If $\nu'/a^2\tau$ (or $\nu'/b^2\tau$) be small, only the less damped range of waves is important, and we then have the approximations

$$\left.\begin{aligned} V_1 &= a \\ q_1 &= 8\pi^2\nu'/3a^2\tau^2 \end{aligned}\right\} (22), \qquad \left.\begin{aligned} V_2 &= b \\ q_2 &= 2\pi^2\nu'/b^2\tau^2 \end{aligned}\right\} (23), \qquad \left.\begin{aligned} V_3 &= 0\cdot 9553b \\ q_3 &= 2\pi^2\nu'/b^2\tau^2 \end{aligned}\right\} (24)$$

The solution given by Dr. Jeffreys (*loc. cit.*, p. 1) for spherical transverse waves is of similar form, as regards velocity and viscous damping, to the approximation (23) for plane distortional waves.

An approximate solution for surface waves on a medium of finite compressibility can be obtained if $\nu'/a^2\tau$ be small. We can then write $\chi = \chi_0 + i\chi_1$, where χ_0 satisfies the equation giving the velocity of ordinary Rayleigh waves (*i.e.* equation (11) with λ' and μ' replaced by λ and μ), and χ_1 is small and of order $\nu\xi c/\mu$, *i.e.*, of order $\nu'/a^2\tau$. The most interesting case is when $a^2 = 3b^2$, which corresponds to the case of $\lambda = \mu$ in a non-viscous medium. Retaining only the lowest powers of quantities of order χ_1 we find that to a first approximation the velocity is unaltered by viscosity. The damping is given by

$$q_3 = 1\cdot 70\pi^2\nu'/b^2\tau^2, \tag{25}$$

and is, therefore, reduced by compressibility. The ratio of horizontal to vertical motion is unaltered, but the elliptic orbit has a small positive rotation in the x, y plane, its inclination being greatest for the shortest wave-lengths.

A rough estimate of the order of the viscosity in the surface layers of the

Earth is suggested by the fact that several seismologists have estimated the value of ϵ in the equation

$$W_2 = W_1 e^{-2\epsilon(\pi R - \Delta)},$$

where Δ is the epicentral distance, R the Earth's radius, and W_1, W_2 are the amplitudes of oscillations in the main shock arriving at the station by the shorter and longer circular arcs joining it to the epicentre. When the distances are measured in kilometres the average value of ϵ is found to be about 0·000139.*

Assuming that the main shock is due to Rayleigh waves, and that the relation $a^2 = 3b^2$ is fulfilled, we have from (25)

$$0{\cdot}000139 = 10^5 q_3/V_3 = 1{\cdot}7 \times 10^5 \pi^2 \nu'/b^3 \sqrt{\eta} \,.\, \tau^2,$$

where $\eta = 0{\cdot}9194$. Taking the value found by Zöppritz and Geiger for the velocity of distortional waves in the upper layers, viz., $b = 4{\cdot}01$ kms. per sec., we find $\nu' = 4{\cdot}91 \times 10^6 \tau^2$. The period of oscillations in the main shock varies from about 12 to 20 secs., so that the viscosity would appear to have an order of 10^8 or 10^9 c.g.s. units. With a viscosity of this order, and the periods commonly observed in earthquakes, the approximate expressions (22) ... (25) would hold good.

§ 5. *The Vibrations of a Visco-Elastic Sphere.*

The effects of viscosity on the vibrations of an incompressible elastic sphere are easily obtained from the solution in spherical harmonics given by Lamb.† We arrive at two equations in $kD/2\pi$ (D being the diameter) which in the case of an elastic incompressible sphere determine the frequencies of vibration. If the sphere be visco-elastic,

$$kD/2\pi = (D/2\pi)\sqrt{\rho p^2/(\mu + ip\nu)} = \gamma, \text{ say,}$$

whence

$$p = \{\pm (2\gamma\pi/D)\sqrt{b^2 - (\gamma\pi\nu'/D)^2}\} + i\,(2\gamma^2\pi^2\nu'/D^2). \tag{26}$$

The vibrations are damped, and the period of any particular mode is increased by viscosity. For any given sphere there is a certain value of γ (say Γ), such that only those modes in which $\gamma < \Gamma$ are vibratory, and thus there is only a finite number of oscillatory modes of any one species. Regarding γ

* See Knott, 'Physics of Earthquake Phenomena,' p. 219; Galitzin, 'Proc. Fifth Intern. Congr. Math.,' vol. I, p. 113; Angenheister, 'Gött. Nach. Ges. Wiss. Math.-phys. Kl.,' pp. 119, 120 (1906).

† 'Proc. Lond. Math. Soc.,' vol. 13 (1882). (If the sphere be compressible, the results given here will still hold good for "vibrations of the first class.")

as a continuously increasing variable we find that the period is a minimum for that mode in which γ lies nearest to $\Gamma/\sqrt{2}$. The damping increases steadily as γ increases, and thus there may be pairs of modes with nearly equal periods but widely differing rates of decay.

In conclusion, I wish to acknowledge my indebtedness to Prof. L. N. G. Filon for introducing me to the equations of motion which form the basis of this paper and for suggesting their application to seismology. My best thanks are due to him for his help and guidance, without which the results could not have been obtained.

Free Motion of a Sphere in a Rotating Liquid at Right Angles to the Axis of Rotation.

By S. F. Grace, University of Liverpool.

(Communicated by G. I. Taylor, F.R.S. Received May 15, 1923.)

§ 1. In a previous paper* the author has discussed the free motion of a sphere in a rotating liquid, when projected parallel to the axis of rotation. The present paper is a discussion on similar lines when the sphere is projected at right angles to the axis. It will often be found convenient to refer to the first paper, and this is done by placing (A) after the reference; thus Diagram I (A) refers to Diagram I of the first paper.

The density of the sphere is taken to be equal to that of the liquid and the motion is a small disturbance from one of uniform rotation like a rigid body; the system is supposed free from bodily forces and is initially disturbed by a motion suddenly communicated to the sphere.

The pressure intensity of the liquid consists of two parts, one depending on the disturbed motion and the other on the distance from the axis; the latter, however, would maintain the sphere in relative rest.

The initial disturbed motion will be irrotational, and since the initial relative motion of the sphere is perpendicular to the axis of rotation the initial disturbed motion of the liquid will be symmetrical with respect to the plane through the centre of the sphere perpendicular to the axis (the equatorial plane of the

* "Free Motion of a Sphere in a Rotating Liquid parallel to the Axis of Rotation," 'Roy. Soc. Proc.,' A, vol. 102, 1922.

sphere), so that the subsequent motion of the centre of the sphere is wholly in this plane and the disturbed motion of the liquid continues to be symmetrical with respect to the plane.

The method of discussion is similar to that adopted in (A) as will be seen in the sequel; it leads to a definite mathematical problem, the solution of which gives the following results :—

The path of the centre of the sphere is a spiral with a definite limiting point. The sphere winds round the limiting point in a direction opposite to the direction of rotation of the liquid while continuously approaching the point, the motion being such that the time of a complete turn round this point tends to become constant and equal to one-half the time of a complete rotation of the undisturbed liquid; the speed consequently tends to zero, but the motion persists longer than when the sphere is projected parallel to the axis of rotation.

The motion of the liquid in the equatorial plane of the sphere exhibits the characteristic noted in (A), viz.: that the motion is practically confined to the neighbourhood of the sphere, though in this case not to such a pronounced degree. The motion at any point is such that the velocity components are oscillatory and tend to zero as we proceed away from the sphere. The actual determination of this motion has involved very heavy numerical work extending over a period of some months' duration. The process necessitated the summation of series, the coefficients in which had to be evaluated to eight figures (an arithmometer being used for this work), and the results were subjected to numerical integration. The final results are exhibited graphically in § 9. The author desires here to express his thanks to Dr. A. T. Doodson for advice regarding this numerical work.

On the axis of the sphere, *i.e.*, the line through the centre of the sphere parallel to the axis of rotation, the motion is wholly perpendicular to the axis and persists with time; it tends to zero as we proceed away from the sphere, the maximum disturbance occurring on the sphere itself, as in the case of the motion in the equatorial plane. At any point the velocity components are oscillatory, the period of oscillation of each tending to become constant at a particular point and varying from an infinitely large value at infinity to one-half the time of a complete rotation of the undisturbed liquid at the sphere. It may be recalled that in (A) the maximum disturbance was found not at the sphere but at some distance away.

At a point on the sphere we find that, relative to the sphere, the tangential velocity of the liquid can be represented as the component in the tangent plane of a certain vector of constant magnitude. This vector is the generator of a

right circular cone drawn inwards from the point in question and having its axis along the radius vector; the generator rotates with constant angular velocity and is initially opposite to the direction of projection of the sphere; the angular velocity is different for different latitudes, varying from a maximum at the poles to zero at the equator. This description also applies to the solution found in (A) but was not there given.

Finally, in addition to the special cases discussed above, general expressions have been obtained for the disturbance at any point.

Combining the results of the two papers we obtain the small general motion of a sphere projected in a rotating liquid with any given initial velocity. The path of the sphere will be a spiral in three dimensions. It must be noted, however, that although the actual motion, initially small, remains small as the time increases, the components of vorticity tend to become large; a case in point is furnished on the axis of the sphere. Thus, parts of the solution are not applicable for large values of time, *i.e.*, a physical restriction is introduced and the solution only gives the true state of the liquid for a restricted time.

The author again wishes to express his thanks to Prof. J. Proudman for the interest he has taken in this work and for much valuable advice on many points which have arisen.

Mathematical Problem.

§ 2. The problem is of the same nature as that for the motion parallel to the axis of rotation.

Using Cartesian axes $Oxyz$, rotating about Oz with constant angular velocity ω, the equations 1, 3, 4 of § 2 (A) hold, but 2 (A) is replaced by

$$lu + mv + nw = l\mathrm{U} + m\mathrm{V}, \tag{2}$$

l, m, n being the direction cosines of the normal to the sphere, and U, V the components of velocity of the sphere in the directions Ox, Oy respectively.

Taking secondary axes as defined in § 2 (A), and assuming u, v, w, U, V and P expressed as power series in time, *i.e.*,

$$u = \sum_{s=0}^{\infty} u_s \frac{(2\omega t)^s}{s!}, \quad v = \sum_{s=0}^{\infty} v_s \frac{(2\omega t)^s}{s!}, \quad w = \sum_{s=0}^{\infty} w_s \frac{(2\omega t)^s}{s!},$$

$$\mathrm{U} = \sum_{s=0}^{\infty} a_s \frac{(2\omega t)^s}{s!}, \quad \mathrm{V} = \sum_{s=0}^{\infty} b_s \frac{(2\omega t)^s}{s!}, \quad \mathrm{P} = 2\omega \sum_{s=0}^{\infty} \mathrm{P}_s \frac{(2\omega t)^s}{s!},$$

where u_s, v_s, w_s, a_s, b_s, P_s are functions of x, y, z only and u_0, v_0, w_0, a_0, b_0 determine the initial state, then 5 (A) holds, but the boundary condition is replaced by

$$lv_s + mv_s + nw_s = la_s + mb_s, \qquad s \geqslant 0.$$

Again, equations 6 (A), 7 (A) and the expressions for u, v, w in terms of P_s are true, and as before our attention is to be concentrated on the sequence P_s.

Thus, from 5 (A) and 7 (A),

$$\nabla^2 P_s = -\frac{\partial^2 P_{s-2}}{\partial z^2}, \qquad s > 0; \tag{8}$$

from 6 (A), since the initial motion is irrotational,

$$\nabla^2 P_0 = 0,$$

and P_{-1}, the velocity potential of the initial motion, satisfies

$$\nabla^2 P_{-1} = 0.$$

At the boundary

$$\frac{\partial P_s}{\partial n} = -la_{s+1} - mb_{s+1} - la_{s-1} - mb_{s-1} - l\frac{\partial P_{s-1}}{\partial y} + m\frac{\partial P_{s-1}}{\partial x} - n\frac{\partial P_{s-2}}{\partial z}, \quad s > 0,$$

$$\frac{\partial P_0}{\partial n} = -la_1 - mb_1 - l\frac{\partial P_{-1}}{\partial y} + m\frac{\partial P_{-1}}{\partial x},$$

$$\frac{\partial P_{-1}}{\partial n} = -la_0 - mb_0.$$

Suppose that initially the sphere is projected with velocity W in the direction Ox, so that

$$a_0 = W, \qquad b_0 = 0,$$

the value of W determining the magnitude of the subsequent disturbance.

Expressions for a_s, b_s in terms of P_s will now be obtained by considering the motion of the sphere.

If X, Y, Z denote the components of resultant pressure on the sphere parallel to the axes

$$-X = \rho \iint (P)_{r=a} \sin\theta \cos\phi \, dS = 2\omega\rho \sum_{s=0}^{\infty} \frac{(2\omega t)^s}{s!} \iint (P_s)_{r=a} \sin\theta \cos\phi \, dS,$$

$$-Y = \rho \iint (P)_{r=a} \sin\theta \sin\phi \, dS = 2\omega\rho \sum_{s=0}^{\infty} \frac{(2\omega t)^s}{s!} \iint (P_s)_{r=a} \sin\theta \sin\phi \, dS,$$

the integrals being taken over the sphere, r, θ, ϕ being the spherical polar co-ordinates of (x, y, z) and a the radius of the sphere.

The symmetry of the disturbance with respect to the direction Oz suggests that there can be no resultant pressure in this direction, so that we take

$$Z = 0.$$

The equations of motion of the sphere now give

$$\sum_{s=0}^{\infty} \frac{(2\omega t)^s}{s\,!} \iint (\mathrm{P}_s)_{r=a} \sin\theta \cos\phi \, d\mathrm{S}$$
$$= -\tfrac{4}{3}\pi a^3 \left\{ \sum_{s=1}^{\infty} a_s \frac{(2\omega t)^{s-1}}{(s-1)\,!} - \sum_{s=0}^{\infty} b_s \frac{(2\omega t)^s}{s\,!} \right\},$$

$$\sum_{s=0}^{\infty} \frac{(2\omega t)^s}{s\,!} \iint (\mathrm{P}_s)_{r=a} \sin\theta \sin\phi \, d\mathrm{S}$$
$$= -\tfrac{4}{3}\pi a^3 \left\{ \sum_{s=1}^{\infty} b_s \frac{(2\omega t)^{s-1}}{(s-1)\,!} + \sum_{s=0}^{\infty} a_s \frac{(2\omega t)^s}{s\,!} \right\},$$

and on comparing the co-efficients of powers of t, we have

$$\left.\begin{aligned} \tfrac{4}{3}\pi a^3 (a_{s+1} - b_s) &= -\iint (\mathrm{P}_s)_{r=a} \sin\theta \cos\phi \, d\mathrm{S}, \\ \tfrac{4}{3}\pi a^3 (b_{s+1} + a_s) &= -\iint (\mathrm{P}_s)_{r=a} \sin\theta \sin\phi \, d\mathrm{S}, \end{aligned}\right\} s \geqslant 0, \tag{9}$$

from which

$$\left.\begin{aligned} -\tfrac{4}{3}\pi a^3 (a_{s+1} + a_{s-1}) &= \iint (\mathrm{P}_s \sin\theta\cos\phi + \mathrm{P}_{s-1} \sin\theta \sin\phi)_{r=a} \, d\mathrm{S}, \\ -\tfrac{4}{3}\pi a^3 (b_{s+1} + b_{s-1}) &= \iint (\mathrm{P}_s \sin\theta\sin\phi - \mathrm{P}_{s-1} \sin\theta \cos\phi)_{r=a} \, d\mathrm{S}, \end{aligned}\right\} \tag{10}$$

for $s > 0$. The boundary conditions may therefore be written

$$\left(\frac{\partial \mathrm{P}_s}{\partial r}\right)_{r=a} = \frac{l}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_s \sin\theta\cos\phi + \mathrm{P}_{s-1}\sin\theta\sin\phi)_{r=a} \, d\mathrm{S}$$
$$+ \frac{m}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_s \sin\theta\sin\phi - \mathrm{P}_{s-1}\sin\theta\cos\phi)_{r=a} \, d\mathrm{S}$$
$$- \left(l \frac{\partial \mathrm{P}_{s-1}}{\partial y} - m \frac{\partial \mathrm{P}_{s-1}}{\partial x} + n \frac{\partial \mathrm{P}_{s-2}}{\partial z} \right)_{r=a}, \quad s > 0, \tag{11}$$

$$\left(\frac{\partial \mathrm{P}_0}{\partial r}\right)_{r=a} = \frac{l}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_0)_{r=a} \sin\theta\cos\phi \, d\mathrm{S} + \frac{m}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_0)_{r=a} \sin\theta\sin\phi \, d\mathrm{S}$$
$$+ m\mathrm{W} - \left(l \frac{\partial \mathrm{P}_{-1}}{\partial y} - m \frac{\partial \mathrm{P}_{-1}}{\partial x} \right)_{r=a},$$

$$\left(\frac{\partial \mathrm{P}_{-1}}{\partial r}\right)_{r=a} = -l\mathrm{W}.$$

Considering

$$\nabla^2 \mathrm{P}_{-1} = 0, \qquad \left(\frac{\partial \mathrm{P}_{-1}}{\partial r}\right)_{r=a} = -\mathrm{W} \sin\theta\cos\phi,$$

the solution is

$$\mathrm{P}_{-1} = \tfrac{1}{2}\mathrm{W}a\,(a/r)^2 \sin\theta\cos\phi.$$

Also

$$\nabla^2 \mathrm{P}_0 = 0,$$

$$\left(\frac{\partial \mathrm{P}_0}{\partial r}\right)_{r=a} = \frac{\sin\theta\cos\phi}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_0)_{r=a} \sin\theta\cos\phi \, d\mathrm{S}$$
$$+ \frac{\sin\theta\sin\phi}{\tfrac{4}{3}\pi a^3} \iint (\mathrm{P}_0)_{r=a} \sin\theta\sin\phi \, d\mathrm{S} + \tfrac{3}{2}\mathrm{W}\sin\theta\sin\phi,$$

from which

$$P_0 = -\tfrac{1}{2}Wa\,(a/r)^2 \sin\theta \sin\phi.$$

Thus the problem reduces to finding a sequence of functions P_s which, for $s > 0$, satisfy (8) and (11), P_0, P_{-1} being given above.

The Solution.

§ 3. The sequence of functions P_s is found to be $(s > 0)$

$$\left.\begin{aligned} P_{2s-1} &= -Wa \sin\theta \cos\phi \sum_{m=1}^{s+1} (a/r)^{2m}\, T_{2m,2s}(\mu), \\ P_{2s} &= Wa \sin\theta \sin\phi \sum_{m=1}^{s+1} (a/r)^{2m}\, T_{2m,2s}(\mu), \end{aligned}\right\} \tag{12}$$

where $\mu = \cos\theta$, and

$$\begin{aligned} T_{2m,2s}(\mu) = {} & (-)^{s-m}\frac{3}{2}\cdot\frac{1.3.5.\dots(2s-1)}{2^s(m-1)!\,(s-m+1)!}\,\frac{(1-\mu^2)^{s-m}}{2m+1}\times \\ & \Big\{1-(2s+1)\,{}^mC_1\mu^2+\frac{(2s+1)(2s+3)}{1.3}\,{}^mC_2\mu^4-\dots \\ & \dots+(-)^k\frac{(2s+1)(2s+3)\dots(2s+2k-1)}{1.3\dots(2k-1)}\,{}^mC_k\mu^{2k}+\dots \\ & \dots+(-)^m\frac{(2s+1)(2s+3)\dots(2s+2m-1)}{1.3\dots(2m-1)}\,\mu^{2m}\Big\} \qquad (13) \\ = {} & (-)^{s-m}\frac{3}{2}\,\frac{\mu(1-\mu^2)^{s-m}}{(2m+1)(m-1)!\,(s-m+1)!}\left(\frac{d}{d\mu^2}\right)^s\{\mu^{2s-1}(1-\mu^2)^m\}. \end{aligned}$$

The method of obtaining this sequence introduces another problem in connection with the motion of a sphere in a rotating liquid, viz.: that of a sphere being towed through the liquid with given velocity. It is hoped in a future paper to give an account of this problem; here we simply verify that the functions (12) do satisfy all the conditions of the problem.

Verification.

§ 4. In the first place it will be shown that, inside the liquid, the assumed form of P_s satisfies (8). For this it is sufficient to show that

$$\left.\begin{aligned} &\nabla^2\left\{a\sin\theta\cos\phi\left(\frac{a}{r}\right)^{2m}T_{2m,2s}(\mu)\right\} \\ &\qquad = -\frac{\partial^2}{\partial z^2}\left\{a\sin\theta\cos\phi\left(\frac{a}{r}\right)^{2m}T_{2m,2s-2}(\mu)\right\}, \\ &\nabla^2\left\{a\sin\theta\sin\phi\left(\frac{a}{r}\right)^{2m}T_{2m,2s}(\mu)\right\} \\ &\qquad = -\frac{\partial^2}{\partial z^2}\left\{a\sin\theta\sin\phi\left(\frac{a}{r}\right)^{2m}T_{2m,2s-2}(\mu)\right\}, \end{aligned}\right\} \tag{14}$$

for $s > 1$, and also that

$$\nabla^2 P_2 = -\frac{\partial^2 P_0}{\partial z^2}, \qquad \nabla^2 P_1 = -\frac{\partial^2 P_{-1}}{\partial z^2}.$$

To prove (14) is equivalent to showing that

$$(1-\mu^2)\frac{\partial^2 T_{2m,2s}}{\partial \mu^2} - 4\mu \frac{\partial T_{2m,2s}}{\partial \mu} + \{2m(2m-1)-2\} T_{2m,2s}$$
$$= -(1-\mu^2)^2 \frac{\partial^2 T_{2m,2s-2}}{\partial \mu^2} + (4m+5)\mu(1-\mu^2)\frac{\partial T_{2m,2s-2}}{\partial \mu}$$
$$- (2m+1)\{(2m+3)\mu^2-1\} T_{2m,2s-2}, \quad (15)$$

so that, denoting $T_{2m,2s}(\mu)$ by

$$(-)^{s-m}\frac{3}{2}\cdot\frac{1.3.5\ldots.(2s-1)}{2^s(m-1)!(s-m+1)!}\frac{p_{2m,2s}}{2m+1},$$

it is required to show that

$$(2s-1)\left[(1-\mu^2)\frac{\partial^2 p_{2m,2s}}{\partial \mu^2} - 4\mu\frac{\partial p_{2m,2s}}{\partial \mu} + \{2m(2m-1)-2\} p_{2m,2s}\right] \quad (16)$$

is identically equal to

$$(2s-2m+2)\left[(1-\mu^2)^2\frac{\partial^2 p_{2m,2s-2}}{\partial \mu^2} - (4m+5)\mu(1-\mu^2)\frac{\partial p_{2m,2s-2}}{\partial \mu}\right.$$
$$\left. + (2m+1)\{(2m+3)\mu^2-1\} p_{2m,2s-2}\right]. \quad (17)$$

Let

$$p_{2m,2s} = (1-\mu^2)^{s-m}\alpha_{2s},$$
$$\frac{\partial p_{2m,2s}}{\partial \mu} = -2(s-m)\mu(1-\mu^2)^{s-m-1}\alpha_{2s} + (1-\mu^2)^{s-m}\alpha'_{2s},$$
$$\frac{\partial^2 p_{2m,2s}}{\partial \mu^2} = 2(s-m)\{(2s-2m-1)\mu^2-1\}(1-\mu^2)^{s-m-2}\alpha_{2s}$$
$$-4(s-m)\mu(1-\mu^2)^{s-m-1}\alpha'_{2s} + (1-\mu^2)^{s-m}\alpha''_{2s};$$

then (16) becomes

$$(2s-1)(1-\mu^2)^{s-m-1}[\{(4s^2-8ms+6s-4m+2)\mu^2+4m^2-2s-2\}\alpha_{2s}$$
$$-4(s-m+1)\mu(1-\mu^2)\alpha'_{2s} + (1-\mu^2)^2\alpha''_{2s}],$$

and (17) becomes

$$(2s-2m+2)(1-\mu^2)^{s-m-1}[(2s-1)\{(2s+1)\mu^2-1\}\alpha_{2s-2}$$
$$-(4s+1)\mu(1-\mu^2)\alpha'_{2s-2} + (1-\mu^2)^2\alpha''_{2s-2}].$$

We show that the expression

$$(2s-1)[\{(4s^2-8ms+6s-4m+2)\mu^2+4m^2-2s-2\}\alpha_{2s}$$
$$-4(s-m+1)\mu(1-\mu^2)\alpha'_{2s} + (1-\mu^2)^2\alpha''_{2s}] \quad (18)$$

is identically equal to

$$(2s-2m+2)[(2s-1)\{(2s+1)\mu^2-1\}\alpha_{2s-2}$$
$$-(4s+1)\mu(1-\mu^2)\alpha'_{2s-2} + (1-\mu^2)^2\alpha''_{2s-2}], \quad (19)$$

by examining the coefficients of μ^{2k} in each and showing that these are equal.

The coefficient of μ^{2k} in (18) is, $(2 < k < m)$,

$$(-)^{k+1}\Big[\frac{(2s-1)(2s+1)\dots(2s+2k+1)}{1.3\dots.(2k+1)}{}^m\mathrm{C}_{k+1}(2k+2)(2k+1)$$
$$+\frac{(2s-1)(2s+1)\dots(2s+2k-1)}{1.3\dots.(2k-1)}{}^m\mathrm{C}_k\{-4m^2+2s+2$$
$$+8k(s-m+1)+4k(2k-1)\}$$
$$+\frac{(2s-1)(2s+1)\dots(2s+2k-3)}{1.3\dots.(2k-3)}{}^m\mathrm{C}_{k-1}\{4s^2-8ms+6s-4m$$
$$+2+4(s-m+1)(2k-2)+(2k-2)(2k-3)\}\Big]$$

$$=(-)^{k+1}\frac{(2s-1)(2s+1)\dots(2s+2k-1)}{1.3\dots.(2k-1)}(2s-2m+2)(2m+1)^{m+1}\mathrm{C}_k,$$

and the coefficient of μ^{2k} in (19) is

$$(-)^{k+1}(2s-2m+2)\Big[\frac{(2s-1)(2s+1)\dots(2s+2k-1)}{1.3\dots.(2k+1)}{}^m\mathrm{C}_{k+1}(2k+2)(2k+1)$$
$$+\frac{(2s-1)(2s+1)\dots(2s+2k-3)}{1.3\dots.(2k-1)}{}^m\mathrm{C}_k\{2s-1$$
$$+2k(4s+1)+4k(2k-1)\}$$
$$+\frac{(2s-1)(2s+1)\dots(2s+2k-5)}{1.3\dots.(2k-3)}{}^m\mathrm{C}_{k-1}\{4s^2-1$$
$$+(4s+1)(2k-2)+(2k-2)(2k-3)\}\Big]$$

$$=(-)^{k+1}\frac{(2s-1)(2s+1)\dots(2s+2k-1)}{1.3\dots.(2k-1)}(2s-2m+2)(2m+1)^{m+1}\mathrm{C}_k.$$

Similarly, by examining the special coefficients of μ^0, μ^2, μ^4, μ^{2m}, μ^{2m+2}, it is seen that they are identical in the two expressions.

Finally (15) is satisfied when $m = s+1$, for in this case $\mathrm{T}_{2m,2s-2}$ is zero and the occurrence of the factor $s-m+1$ in (18) causes the left-hand side of (15) to vanish also.

Taking now

$$\mathrm{P}_1 = -\mathrm{W}a\sin\theta\cos\phi\left\{\frac{a^2}{r^2}\frac{1}{4}(1-3\mu^2)+\frac{a^4}{r^4}\frac{3}{20}(5\mu^2-1)\right\},$$

$$\mathrm{P}_2 = \mathrm{W}a\sin\theta\sin\phi\left\{\frac{a^2}{r^2}\frac{1}{4}(1-3\mu^2)+\frac{a^4}{r^4}\frac{3}{20}(5\mu^2-1)\right\},$$

obtained by substituting $s = 1$ in (12) and (13), it is easily verified that

$$\nabla^2\mathrm{P}_1 = -\frac{\partial^2\mathrm{P}_{-1}}{\partial z^2},\qquad \nabla^2\mathrm{P}_2 = -\frac{\partial^2\mathrm{P}_0}{\partial z^2}.$$

It now remains to show that the assumed form of P_s satisfies the boundary conditions.

First, supposing $s > 1$, we have

$$(P_{2s})_{r=a} = \mathrm{W}a \sin\theta \sin\phi \sum_{m=1}^{s+1} T_{2m,2s}$$

$$= \frac{3}{2} \mathrm{W}a\mu \sin\theta \sin\phi \sum_{m=1}^{s+1} (-)^{s-m} \frac{(1-\mu^2)^{s-m}}{(2m+1)(m-1)!(s-m+1)!} \cdot \left(\frac{d}{d\mu^2}\right)^s \{\mu^{2s-1}(1-\mu^2)^m\}$$

$$\left.\begin{aligned} &= (-)^{s-1} \frac{3}{2} \frac{\mathrm{W}a \sin\theta \sin\phi}{(2s+1)(2s+3)}, \\ (P_{2s-1})_{r=a} &= (-)^s \frac{3}{2} \frac{\mathrm{W}a \sin\theta \cos\phi}{(2s+1)(2s+3)}. \end{aligned}\right\} \quad (20)$$

Also

$$\left(\frac{\partial P_{2s}}{\partial r}\right)_{r=a} = -\mathrm{W} \sin\theta \sin\phi \sum_{m=1}^{s+1} 2m T_{2m,2s}$$

$$= -\frac{3}{2} \mathrm{W}\mu \sin\theta \sin\phi \sum_{m=1}^{s+1} (-)^{s-m} \frac{2m(1-\mu^2)^{s-m}}{(2m+1)(m-1)!(s-m+1)!} \cdot \left(\frac{d}{d\mu^2}\right)^s \{\mu^{2s-1}(1-\mu^2)^m\}$$

$$\left.\begin{aligned} &= (-)^s \frac{3}{2} \mathrm{W} \sin\theta \sin\phi \left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}, \\ \left(\frac{\partial P_{2s-1}}{\partial r}\right)_{r=a} &= (-)^{s-1} \frac{3}{2} \mathrm{W} \sin\theta \cos\phi \left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}. \end{aligned}\right\} \quad (21)$$

Again, since

$$-l\frac{\partial}{\partial y} + m\frac{\partial}{\partial x} = -\frac{\partial}{r\,\partial\phi},$$

it follows that

$$\left(-l\frac{\partial P_{2s}}{\partial y} + m\frac{\partial P_{2s}}{\partial x}\right)_{r=a} = (-)^s \frac{3}{2} \frac{\mathrm{W} \sin\theta \cos\phi}{(2s+1)(2s+3)},$$

$$\left(-l\frac{\partial P_{2s-1}}{\partial y} + m\frac{\partial P_{2s-1}}{\partial x}\right)_{r=a} = (-)^s \frac{3}{2} \frac{\mathrm{W} \sin\theta \sin\phi}{(2s+1)(2s+3)}.$$

Finally, using

$$n\frac{\partial}{\partial z} = \cos^2\theta \frac{\partial}{\partial r} - \frac{\cos\theta \sin\theta}{r} \frac{\partial}{\partial\theta},$$

we find that

$$\left.\begin{aligned} \left(\frac{\partial P_{2s}}{\partial\theta}\right)_{r=a} &= (-)^{s-1} \frac{3}{2} \frac{\mathrm{W}a \cos\theta \sin\phi}{(2s+1)(2s+3)}, \\ \left(\frac{\partial P_{2s-1}}{\partial\theta}\right)_{r=a} &= (-)^s \frac{3}{2} \frac{\mathrm{W}a \cos\theta \cos\phi}{(2s+1)(2s+3)}, \end{aligned}\right\} \quad (22)$$

so that, from (21) and (22),

$$\left(n\frac{\partial P_{2s}}{\partial z}\right)_{r=a} = (-)^s \frac{3}{2} W\mu^{2s+2} \sin\theta \sin\phi,$$

$$\left(n\frac{\partial P_{2s-1}}{\partial z}\right)_{r=a} = (-)^{s-1} \frac{3}{2} W\mu^{2s+2} \sin\theta \cos\phi.$$

It now follows that

$$\frac{\sin\theta\cos\phi}{\frac{4}{3}\pi a^3}\iint (P_{2s}\sin\theta\cos\phi + P_{2s-1}\sin\theta\sin\phi)_{r=a}\,dS$$
$$+\frac{\sin\theta\sin\phi}{\frac{4}{3}\pi a^3}\iint (P_{2s}\sin\theta\sin\phi - P_{2s-1}\sin\theta\cos\phi)_{r=a}\,dS$$
$$-\left(l\frac{\partial P_{2s-1}}{\partial y} - m\frac{\partial P_{2s-1}}{\partial x} + n\frac{\partial P_{2s-2}}{\partial z}\right)_{r=a}$$
$$= (-)^{s-1}\frac{3}{2}\frac{W\sin\theta\sin\phi}{(2s+1)(2s+3)} - (-)^{s-1}\frac{3}{2}W\mu^{2s}\sin\theta\sin\phi$$
$$= \left(\frac{\partial P_{2s}}{\partial r}\right)_{r=a},$$

and that

$$\frac{\sin\theta\cos\phi}{\frac{4}{3}\pi a^3}\iint (P_{2s-1}\sin\theta\cos\phi + P_{2s-2}\sin\theta\sin\phi)_{r=a}\,dS$$
$$+\frac{\sin\theta\sin\phi}{\frac{4}{3}\pi a^3}\iint (P_{2s-1}\sin\theta\sin\phi - P_{2s-2}\sin\theta\cos\phi)_{r=a}\,dS$$
$$-\left(l\frac{\partial P_{2s-2}}{\partial y} - m\frac{\partial P_{2s-2}}{\partial x} + n\frac{\partial P_{2s-3}}{\partial z}\right)_{r=a}$$
$$= \left(\frac{\partial P_{2s-1}}{\partial r}\right)_{r=a}.$$

Finally, it is easily verified that the boundary condition (11) is also satisfied when $s = 1, 2$, thus completing the verification that the functions P_s, given in § 3, satisfy the conditions of the problem.

Convergence.

§ 5. Examining briefly the convergence of the series for u, v, w and P in terms of P_s, we find that for $m \leqslant s$

$$|T_{2m,2s}(\mu)| < \frac{3}{2}\frac{1.3.5....(2s-1)}{(2m+1)2^s(m-1)!(s-m+1)!}\left\{1+(2s+1)\,{}^m C_1 + \frac{(2s+1)(2s+3)}{1.3}\,{}^m C_2 + \ldots\right\}$$
$$< \frac{3}{2}\frac{(2m+3)(2m+5)\ldots(2s+2m-1)}{2^s(m-1)!(s-m+1)!}\{1+{}^m C_1+{}^m C_2+\ldots\}$$
$$< \frac{3}{2}\cdot\frac{(s+2)(s+3)\ldots 2s}{2(m-1)!(s-m+1)!}2^m$$
$$< \frac{3}{2}\frac{2^{m-1}}{(m-1)!}(s+2)(s+3)\ldots 2s,$$

whereas

$$T_{2s+2,\,2s}(\mu) = -\frac{3}{2}\cdot\frac{1.3\ldots.(2s-1)}{2^s.\,s!\,(2s+3)}\frac{1}{1-\mu^2}\Big\{1-(2s+1)^{s+1}C_1\mu^2$$

$$+\frac{(2s+1)(2s+3)}{1.3}{}^{s+1}C_2\mu^4-\ldots\Big\}$$

$$= -\frac{3}{2}\cdot\frac{1.3\ldots.(2s-1)}{2^s.\,s!\,(2s+3)}\Big\{1-(2s+3)^sC_1\mu^2$$

$$+\frac{(2s+3)(2s+5)}{1.3}{}^sC_2\mu^4-\ldots\Big\}$$

so that

$$|T_{2s+2,\,2s}(\mu)| < \frac{3}{2}\cdot\frac{2^s}{s!}(s+2)(s+3)\ldots 2s.$$

Thus

$$|P_{2s}| < Wa\sum_{m=1}^{s+1}\frac{3}{2}(s+2)(s+3)\ldots 2s\;\frac{2^{m-1}}{(m-1)!}$$

$$< 12Wa\,(s+2)(s+3)\ldots 2s,$$

and $$|P_{2s-1}| < 12Wa\,(s+2)(s+3)\ldots 2s,$$

from which

$$\frac{|P_{2s}|}{2s!} < 12Wa\,\frac{(s+2)(s+3)\ldots 2s}{2s!} = \frac{12Wa}{(s+1)!},$$

and

$$\frac{|P_{2s-1}|}{(2s-1)!} < \frac{24Wa}{s!}.$$

The series $2\omega\sum_{s=0}^{\infty}P_s(2\omega t)^s/s!$, for P is therefore absolutely convergent for all finite values of t.

Examining the gradient of P, we find

$$\left|\frac{\partial P_{2s}}{\partial r}\right| < (2s+2)\,|P_{2s}|,\qquad \left|\frac{\partial P_{2s-1}}{\partial r}\right| < (2s+2)\,|P_{2s-1}|,$$

$$\left|\frac{\partial P_{2s}}{\partial\phi}\right| \leqslant |P_{2s}|\qquad,\qquad \left|\frac{\partial P_{2s-1}}{\partial\phi}\right| \leqslant |P_{2s-1}|\qquad,$$

$$\left|\frac{\partial P_{2s}}{\partial\theta}\right| < (2s+1)\,|P_{2s}|,\qquad \left|\frac{\partial P_{2s-1}}{\partial\theta}\right| < (2s+1)\,|P_{2s-1}|,$$

so that

$$|\text{Gradient of } P_{2s}| < 4(s+1)\,|P_{2s}|,$$
$$|\text{Gradient of } P_{2s-1}| < 4(s+1)\,|P_{2s-1}|,$$

from which it may be shown that the series for u, v, w, in terms of P_s, are absolutely convergent for finite values of t.

The Motion of the Sphere.

§ 6. To obtain the motion of the sphere we consider the expressions for the coefficients a_s, b_s given by (9) and (10).

Considering ($s > 0$)

$$-\tfrac{4}{3}\pi a^3 (a_{s+1} + a_{s-1}) = \iint (\mathrm{P}_s \sin\theta \cos\phi + \mathrm{P}_{s-1} \sin\theta \sin\phi)_{r=a}\, d\mathrm{S},$$

we see that

$$a_{2s+1} + a_{2s-1} = 0,$$

and from (9)

$$-\tfrac{4}{3}\pi a^3 (a_1 - b_0) = \iint (\mathrm{P}_0)'_{r=a} \sin\theta \cos\phi \, d\mathrm{S} = 0,$$

and since b_0 is zero it follows that

$$a_{2s+1} = 0, \qquad s \geqslant 0.$$

Again, from (9)

$$\tfrac{4}{3}\pi a^3 b_{2s} = \iint (\mathrm{P}_{2s})_{r=a} \sin\theta \cos\phi \, d\mathrm{S} = 0,$$

hence

$$b_{2s} = 0, \qquad s \geqslant 0.$$

Taking now

$$-\tfrac{4}{3}\pi a^3 (a_{2s} + a_{2s-2}) = \iint (\mathrm{P}_{2s-1} \sin\theta \cos\phi + \mathrm{P}_{2s-2} \sin\theta \sin\phi)_{r=a}\, d\mathrm{S}$$
$$= (-)^s \frac{\tfrac{4}{3}\pi a^3 \,.\, 3\mathrm{W}}{(2s-1)(2s+3)},$$

we have

$$a_{2s} + (-)^{s-1}\mathrm{W} = (-)^{s-1} 3\mathrm{W} \sum_{n=1}^{s} \frac{1}{(2n-1)(2n+3)},$$

or

$$a_{2s} = (-)^s 3\mathrm{W} \frac{s+1}{(2s+1)(2s+3)}, \qquad s \geqslant 0,$$

and

$$\tfrac{4}{3}\pi a^3 b_{2s+1} = -\tfrac{4}{3}\pi a^3 a_{2s} - \iint (\mathrm{P}_{2s})_{r=a} \sin\theta \sin\phi \, d\mathrm{S},$$

or

$$b_{2s+1} = (-)^{s+1} \frac{3\mathrm{W}}{2(2s+3)}, \qquad s \geqslant 0.$$

We may now obtain expressions for U, V, the components of velocity of the centre of the sphere, thus

$$\mathrm{U} = \sum_{s=0}^{\infty} a_s \frac{(2\omega t)^s}{s!} = 3\mathrm{W} \sum_{s=0}^{\infty} (-)^s \frac{s+1}{(2s+1)(2s+3)} \frac{(2\omega t)^{2s}}{2s!}$$
$$= \frac{3}{2}\mathrm{W} \left\{ \frac{\sin 2\omega t}{2\omega t} + \frac{\cos 2\omega t}{(2\omega t)^2} - \frac{\sin 2\omega t}{(2\omega t)^3} \right\},$$

or, adopting the notation

$$\mathrm{S}_n(x) = x^{n+1} \left(-\frac{1}{x} \cdot \frac{d}{dx} \right)^n \frac{\sin x}{x},$$

and letting $S_n'(x)$ denote the differential coefficient with respect to x, we have

$$U = \frac{3W}{2} \cdot \frac{S_1'(2\omega t)}{2\omega t}.$$

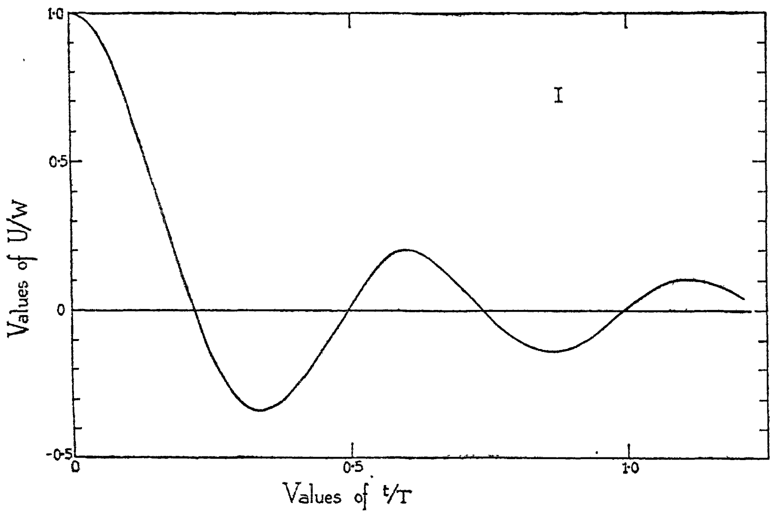
Again

$$V = \sum_{s=0}^{\infty} b_s \frac{(2\omega t)^s}{s!} = \frac{3}{2} W \sum_{s=0}^{\infty} (-)^{s+1} \frac{(2\omega t)^{2s+1}}{(2s+3)(2s+1)!}$$

$$= \frac{3}{2} W \left\{ \frac{\cos 2\omega t}{2\omega t} - \frac{\sin 2\omega t}{(2\omega t)^2} \right\}$$

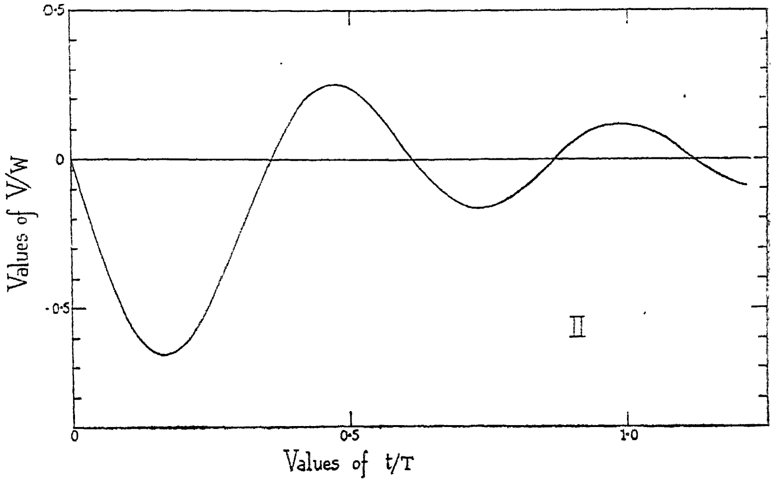
$$= -\frac{3W}{2} \cdot \frac{S_1(2\omega t)}{2\omega t}.$$

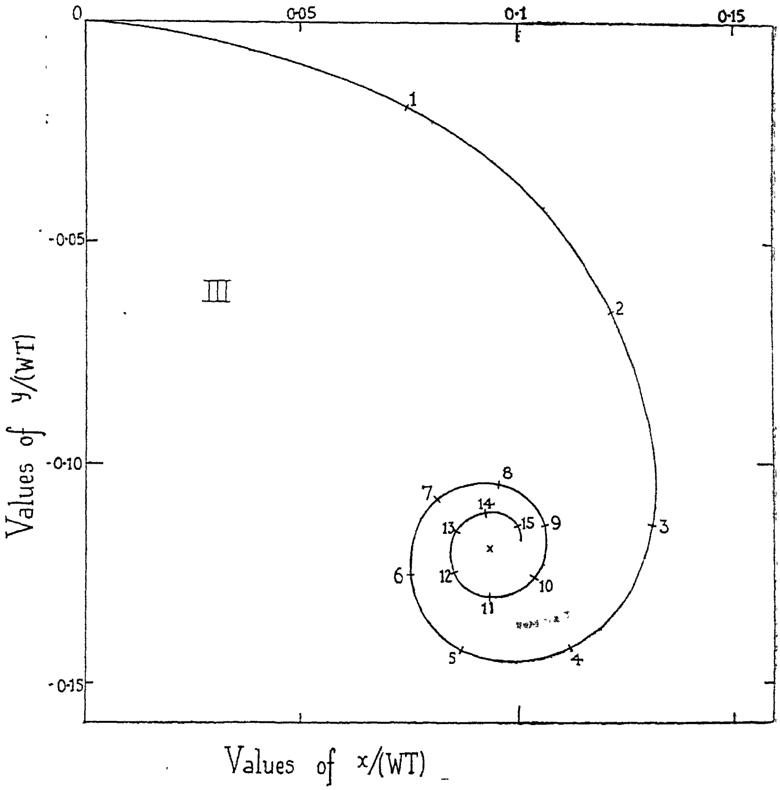
The Diagrams I and II indicate the variations of the functions U and V with time; they are obtained by plotting the values of U/W, V/W respectively against those of t/T, where T is the time of a complete revolution of the undisturbed liquid.



It is interesting also to compare these diagrams with Diagram I (A), which represents the velocity of the sphere in its motion parallel to the axis of rotation of the liquid.

In these diagrams we observe the oscillatory nature of the velocity components; the amplitudes tend to zero as t increases and the periods tend to the constant value $\frac{1}{2}$T. In the case under discussion, however, the speed tends to zero as $1/2\omega t$, whereas in the motion parallel to the axis the order is $1/(2\omega t)^2$.


0·5
0
-0·5
Values of V/W
II
0
0·5
1·0
Values of t/T


0
0·05
0·1
0·15
-0·05
-0·10
-0·15
III
Values of y/(WT)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Values of x/(WT)

The expressions

$$x = \int_0^t \mathrm{U}\, dt = \frac{3}{2}\mathrm{W}\int_0^t \left\{ \frac{\sin 2\omega t}{2\omega t} + \frac{\cos 2\omega t}{(2\omega t)^2} - \frac{\sin 2\omega t}{(2\omega t)^3} \right\} dt$$

$$= \frac{3\mathrm{W}}{8\omega} \cdot \frac{\mathrm{S}_1(2\omega t)}{2\omega t} + \frac{3\mathrm{W}}{4}\int_0^t \frac{\sin 2\omega t}{2\omega t} dt,$$

$$y = \int_0^t \mathrm{V}\, dt = \frac{3}{2}\mathrm{W}\int_0^t \left\{ \frac{\cos 2\omega t}{2\omega t} - \frac{\sin 2\omega t}{(2\omega t)^2} \right\} dt$$

$$= \frac{3\mathrm{W}}{4\omega}\left(\frac{\sin 2\omega t}{2\omega t} - 1\right),$$

give the position of the centre of the sphere at time t; from them Diagram III has been constructed to indicate the form of the path of the sphere from $t = 0$ to $1 \cdot 2\mathrm{T}$. The points 1, 2, 3, ... 15 represent the positions of the centre of the sphere for $2\omega t = 1, 2, 3, \ldots 15$ respectively.

The path is seen to take the form of a spiral, the pole of which is at the point whose co-ordinates are

$$x = \frac{3\mathrm{W}}{4}\int_0^\infty \frac{\sin 2\omega t}{2\omega t} dt = \frac{3\pi \mathrm{W}}{16\omega} = \frac{3}{32}\mathrm{WT} = 0{\cdot}094\mathrm{WT},$$

$$y = -\frac{3\mathrm{W}}{4\omega} = -\frac{3}{8\pi}\mathrm{WT} = -0{\cdot}119\ \mathrm{WT}.$$

The sphere revolves about this limiting position in a direction opposite to the rotation of the undisturbed liquid, the period of a revolution tending to become $\frac{1}{2}$ T; the distance of the centre of the sphere from the limiting position continually decreases, the order of decrease being ultimately $1/2\omega t$.

Velocity of the Liquid.

§ 7. Considering for a moment the general motion of the liquid we see from 7 (A) that

$$u_{2s+1} + u_{2s-1} = -\frac{\partial \mathrm{P}_{2s}}{\partial x} - \frac{\partial \mathrm{P}_{2s-1}}{\partial y}, \qquad s > 0,$$

and, on substituting for P_{2s} and P_{2s-1}, we obtain

$$u_{2s+1} + u_{2s-1} = 0, \qquad s > 0,$$

and since

$$u_1 = v_0 - \frac{\partial \mathrm{P}_0}{\partial x} = -\frac{\partial \mathrm{P}_{-1}}{\partial y} - \frac{\partial \mathrm{P}_0}{\partial x} = 0,$$

we have

$$u_{2s+1} = 0, \qquad s \geqslant 0,$$

and

$$v_{2s} = -\frac{\partial \mathrm{P}_{2s-1}}{\partial y} = \frac{\partial \mathrm{P}_{2s}}{\partial x}, \qquad s \geqslant 0.$$

Velocity of the Liquid on the Axis of the Sphere.

§ 8. On the axis of the sphere θ is zero or π, so that

$$P_{2s} = P_{2s-1} = 0, \qquad s \geqslant 0,$$

and w is zero also, or the motion is wholly perpendicular to the axis. Further since the motion is symmetrical with respect to the equatorial plane, it is only necessary to consider one of the values of θ, say $\theta = 0$.

Putting $\lambda = a/r$, we have

$$v_{2s} = -\left(\frac{\partial P_{2s-1}}{\partial y}\right)_{\theta=0} = -\frac{\sin\phi}{r}\left(\frac{\partial P_{2s-1}}{\partial\theta}\right)_{\theta=0} - \left(\frac{\cos\phi}{r\sin\theta}\frac{\partial P_{2s-1}}{\partial\phi}\right)_{\theta=0}$$
$$= 0, \qquad s \geqslant 0.$$

Again, from 7 (A),

$$v_{2s+1} + v_{2s-1} = -\frac{\sin\phi}{r}\left(\frac{\partial P_{2s}}{\partial\theta}\right)_{\theta=0} - \left(\frac{\cos\phi}{r\sin\theta}\frac{\partial P_{2s}}{\partial\phi}\right)_{\theta=0}$$
$$+\frac{\cos\phi}{r}\left(\frac{\partial P_{2s-1}}{\partial\theta}\right)_{\theta=0} - \left(\frac{\sin\phi}{r\sin\theta}\frac{\partial P_{2s-1}}{\partial\phi}\right)_{\theta=0}$$
$$= -2W\lambda\left(\lambda^{2s}T_{2s,2s} + \lambda^{2s+2}T_{2s+2,2s}\right)_{\theta=0}, \qquad s > 0.$$

But

$$(T_{2s,2s})_{\theta=0} = \frac{3}{2}\cdot\frac{1.3.5\ldots.(2s-1)}{(2s+1)\,2^s\,(s-1)!}\left\{1-(2s+1)\,{}^sC_1 + \frac{(2s+1)(2s+3)}{1.3}\,{}^sC_2 - \ldots\right\}$$
$$= (-)^s\frac{3s}{2(2s+1)},$$

$$(T_{2s+2,2s})_{\theta=0} = -\frac{3}{2}\cdot\frac{1.3.5\ldots.(2s-1)}{(2s+3)\,2^s\,.\,s!}\left\{1-(2s+3)\,{}^sC_1 + \frac{(2s+3)(2s+5)}{1.3}\,{}^sC_2 - \ldots\right\}$$
$$= (-)^{s+1}\frac{3(s+1)}{2(2s+3)}.$$

Hence

$$v_{2s+1} + v_{2s-1} = (-)^{s+1}3W\left(\frac{s}{2s+1}\lambda^{2s+1} - \frac{s+1}{2s+3}\lambda^{2s+3}\right),$$

and from this sequence

$$v_{2s+1} + (-)^{s+1}v_1 = (-)^{s+1}3W\left(\frac{1}{3}\lambda^3 - \frac{s+1}{2s+3}\lambda^{2s+3}\right),$$

so that

$$v_{2s+1} = (-)^s 3W\frac{(s+1)\,\lambda^{2s+3}}{2s+3}, \qquad s \geqslant 0.$$

Again

$$u_{2s} = v_{2s-1} - \left(\frac{\partial P_{2s-1}}{\partial x}\right)_{\theta=0}$$

$$= (-)^{s-1}\, 3W \frac{s\lambda^{2s+1}}{2s+1} + (-)^s \frac{3W}{2}\left(\frac{s}{2s+1}\lambda^{2s+1} - \frac{s+1}{2s+3}\lambda^{2s+3}\right)$$

$$= (-)^{s+1}\frac{3W}{2}\left(\frac{s}{2s+1}\lambda^{2s+1} + \frac{s+1}{2s+3}\lambda^{2s+3}\right), \qquad s \geqslant 0.$$

Hence

$$u = \frac{3W}{2}\sum_{s=0}^{\infty}(-)^{s+1}\left(\frac{s}{2s+1}\lambda^{2s+1} + \frac{s+1}{2s+3}\lambda^{2s+3}\right)\frac{(2\omega t)^{2s}}{2s\,!}$$

$$= \frac{3}{4}W\lambda\left(\frac{\sin 2\lambda\omega t}{2\lambda\omega t} - \cos 2\lambda\omega t\right)\left[1 + \lambda^2\left\{1 - \frac{2}{(2\lambda\omega t)^2}\right\}\right]$$

$$= \frac{3W}{4}\left\{\frac{a}{r} + \frac{a^3}{r^3} - 2\frac{a}{r}\frac{1}{(2\omega t)^2}\right\}S_1\left(\frac{2a\omega t}{r}\right),$$

$$v = 3W\sum_{s=0}^{\infty}(-)^s\frac{(s+1)\,\lambda^{2s+3}}{2s+3}\frac{(2\omega t)^{2s+1}}{(2s+1)\,!}$$

$$= \frac{3}{2}W\lambda^2\left\{\sin 2\lambda\omega t + \frac{\cos 2\lambda\omega t}{2\lambda\omega t} - \frac{\sin 2\lambda\omega t}{(2\lambda\omega t)^2}\right\}$$

$$= \frac{3W}{2}\frac{a^2}{r^2}S'_1\left(\frac{2a\omega t}{r}\right).$$

Diagrams IV and V respectively represent the variations of the functions u, v with r and t. In IV the values of u/W are plotted against those of r/a; the separate curves 0, 1, 2, ... 10 correspond respectively to times given by $2\omega t = 0, 1, 2, \ldots 10$, $2\omega t = 10$ being roughly equivalent to $t = 0{\cdot}8\,T$. Diagram V is constructed in a similar manner with the ratios v/W.

For large values of t we may take

$$u = -\tfrac{3}{4}W(\lambda + \lambda^3)\cos 2\lambda\omega t, \qquad v = \tfrac{3}{2}W\lambda^2 \sin 2\lambda\omega t,$$

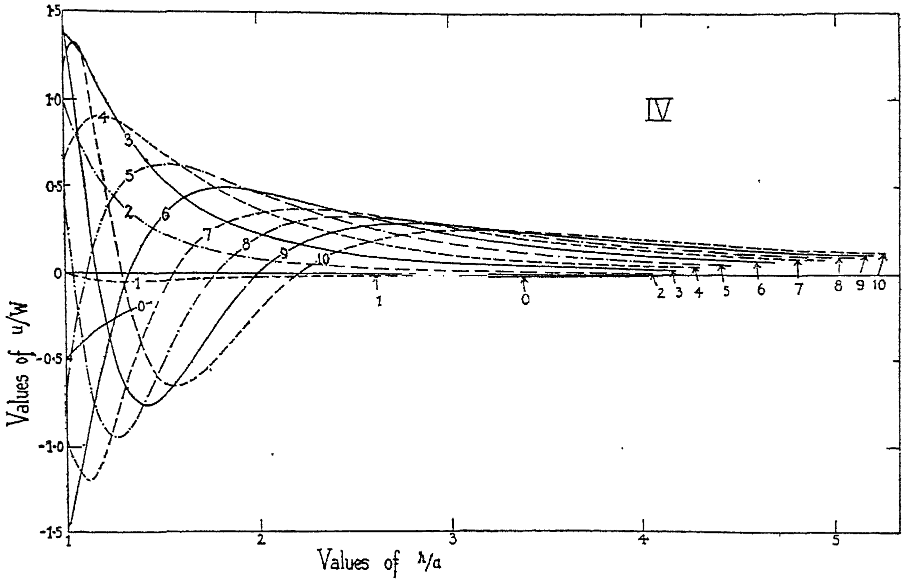
showing that the motion on the axis persists with time; at any point the velocity components are oscillatory, the periods tending to the value $T/2\lambda$. At a great distance from the sphere, *i.e.*, for small values of λ, we may further take

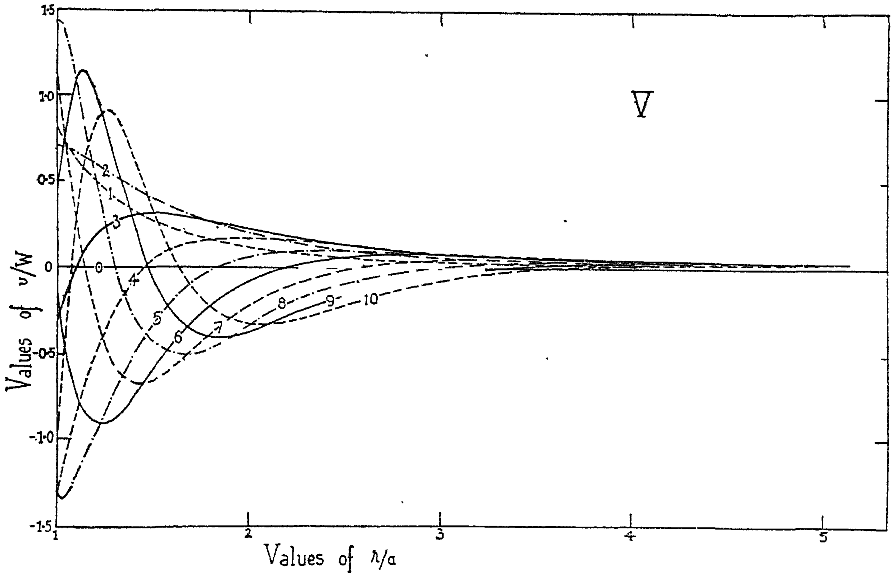
$$u = -\tfrac{3}{4}W\lambda\cos 2\lambda\omega t, \qquad v = 0,$$

since the value of v depends on λ^2.

The magnitude of the disturbance tends to zero as the distance from the sphere increases, the maximum disturbance occurring on the sphere.

If we compare the above expressions for u, v with 21 (A), which gives the velocity of the liquid along the axis for the parallel motion, and compare also





IV, V with II (A), we note the same general characteristics, but in the latter case the maximum disturbance takes place in the neighbourhood of $r = 1 \cdot 7a$.

Velocity of the Liquid on the Equatorial Plane of the Sphere.

§ 9. On the equatorial plane we have $\theta = \frac{1}{2}\pi$, so that

$$w_{2s+1} = -\left(\frac{\partial P_{2s}}{\partial z}\right)_{\mu=0} = \frac{1}{r}\left(\frac{\partial P_{2s}}{\partial \theta}\right)_{\mu=0} = 0,$$

$$w_{2s} = -\left(\frac{\partial P_{2s-1}}{\partial z}\right)_{\mu=0} = 0,$$

and there is no motion of the liquid across the plane.

Again

$$v_{2s} = -\sin\phi\left(\frac{\partial P_{2s-1}}{\partial r}\right)_{\mu=0} - \frac{\cos\phi}{r}\left(\frac{\partial P_{2s-1}}{\partial \phi}\right)_{\mu=0}$$

$$= -\frac{3}{2}W\sin\phi\cos\phi\sum_{m=1}^{s+1}(-)^{s-m}\frac{1.3.5\ldots(2s-1)}{2^s(m-1)!\,(s-m+1)!}\lambda^{2m+1}$$

$$= (-)^s\frac{3W}{2}\frac{1.3.5\ldots(2s-1)}{2^s.s!}\lambda^3(1-\lambda^2)^s\sin\phi\cos\phi, \qquad s>0,$$

$$v_0 = \tfrac{3}{2}W\lambda^3\sin\phi\cos\phi,$$

and

$$v_{2s+1}+v_{2s-1} = \left(-\sin\phi\frac{\partial P_{2s}}{\partial r} - \frac{\cos\phi}{r}\frac{\partial P_{2s}}{\partial\phi} + \cos\phi\frac{\partial P_{2s-1}}{\partial r} - \frac{\sin\phi}{r}\cdot\frac{\partial P_{2s-1}}{\partial\phi}\right)_{\mu=0}$$

$$= (-)^{s+1}\frac{3W}{2}\frac{1.3\ldots(2s-1)}{2^s.s!}\sum_{m=1}^{s+1}(-)^{m-1}\frac{2m-1}{2m+1}{}^sC_{m-1}\lambda^{2m+1}$$

$$= (-)^{s+1}\frac{3W}{2}\frac{1.3\ldots(2s-1)}{2^s.s!}\left\{\lambda^3(1-\lambda^2)^s - 2\int_0^\lambda\lambda^2(1-\lambda^2)^s d\lambda\right\},$$

$$s>0,$$

$$v_1 = -\tfrac{3}{2}W\left\{\lambda^3 - 2\int_0^\lambda\lambda^2 d\lambda\right\},$$

so that, $s>0$,

$$v_{2s+1} = (-)^{s+1}\frac{3}{2}W\lambda^3\left\{1+\frac{1}{2}(1-\lambda^2)+\frac{1.3}{2.4}(1-\lambda^2)^2+\ldots + \frac{1.3\ldots(2s-1)}{2.4\ldots 2s}(1-\lambda^2)^s\right\}$$

$$-(-)^{s+1}3W\int_0^\lambda\lambda^2\left\{1+\frac{1}{2}(1-\lambda^2)+\frac{1.3}{2.4}(1-\lambda^2)^2+\ldots + \frac{1.3\ldots(2s-1)}{2.4\ldots 2s}(1-\lambda^2)^s\right\}d\lambda.$$

Or, putting

$$f_s(\lambda) = 1+\frac{1}{2}(1-\lambda^2)+\frac{1.3}{2.4}(1-\lambda^2)^2+\ldots+\frac{1.3\ldots(2s-1)}{2.4\ldots 2s}(1-\lambda^2)^s,$$

we have

$$v_{2s+1} = (-)^{s+1}\tfrac{3}{2}W\left\{\lambda^3 f_s(\lambda) - 2\int_0^\lambda\lambda^2 f_s(\lambda)\,d\lambda\right\}, \qquad s>0.$$

Considering the coefficients u_{2s}, we have

$$u_{2s} = -v_{2s+1} - \left(\sin\phi\frac{\partial P_{2s}}{\partial r} + \frac{\cos\phi}{r}\frac{\partial P_{2s}}{\partial\phi}\right)_{\mu=0}$$

$$= -v_{2s+1} + \frac{3}{2}W\sin^2\phi\sum_{m=1}^{s+1}(-)^{s-m}\frac{1.3\ldots(2s-1)}{2^s(m-1)!(s-m+1)!}\frac{2m}{2m+1}\lambda^{2m+1}$$

$$-\frac{3}{2}W\cos^2\phi\sum_{m=1}^{s+1}(-)^{s-m}\frac{1.3\ldots(2s-1)}{2^s(m-1)!(s-m+1)!}\frac{1}{2m+1}\lambda^{2m+1}$$

$$= (-)^s\frac{3}{2}W\left\{\lambda^3 f_s(\lambda)' - 2\int_0^\lambda \lambda^2 f_s(\lambda)\,d\lambda\right\}$$

$$-(-)^s\frac{3}{2}W\sin^2\phi\frac{1.3\ldots(2s-1)}{2^s.s!}\lambda^3(1-\lambda^2)^s$$

$$+(-)^s\frac{3}{2}W\frac{1.3\ldots(2s-1)}{2^s.s!}\int_0^\lambda\lambda^2(1-\lambda^2)^s\,d\lambda, \qquad s>0,$$

with

$$u_0 = \tfrac{3}{2}W\lambda^3\cos^2\phi - \tfrac{1}{2}W\lambda^3.$$

From these expressions for u_s, v_s we find, taking $f_0(\lambda) = 1$, that

$$u = \sum_{s=0}^{\infty} u_s\frac{(2\omega t)^s}{s!}$$

$$= \frac{3W}{2}\sum_{s=0}^{\infty}(-)^s\lambda^3 f_s(\lambda)\frac{(2\omega t)^{2s}}{2s!} - 3W\int_0^\lambda\sum_{s=0}^{\infty}(-)^s\lambda^2 f_s(\lambda)\frac{(2\omega t)^{2s}}{2s!}d\lambda$$

$$-\tfrac{3}{2}W\lambda^3\sin^2\phi\,.\,J_0\{2\omega t\surd(1-\lambda^2)\} + \tfrac{3}{2}W\int_0^\lambda\lambda^2.J_0\{2\omega t\surd(1-\lambda^2)\}\,d\lambda, \quad (23)$$

and

$$v = \frac{3W}{2}\sum_{s=0}^{\infty}(-)^{s+1}\lambda^3 f_s(\lambda)\frac{(2\omega t)^{2s+1}}{(2s+1)!}$$

$$-3W\int_0^\lambda\sum_{s=0}^{\infty}(-)^{s+1}\lambda^2 f_s(\lambda)\frac{(2\omega t)^{2s+1}}{(2s+1)!}d\lambda$$

$$+\tfrac{3}{2}W\lambda^3\sin\phi\cos\phi\,.\,J_0\{2\omega t\surd(1-\lambda^2)\}, \quad (24)$$

where $J_0\{2\omega t\surd(1-\lambda^2)\}$ denotes the Bessel function of zero order.

For convenience in the discussion of the expressions (23) and (24), we write

$$u = u_1 - \tfrac{3}{2}W\lambda^3\sin^2\phi\,.\,J_0\{2\omega t\surd(1-\lambda^2)\},$$
$$v = v_1 + \tfrac{3}{2}W\lambda^3\sin\phi\cos\phi\,.\,J_0\{2\omega t\surd(1-\lambda^2)\},$$

u_1 being the portion of the expression for u which is independent of ϕ, v_1 the portion of v independent of ϕ.

From (23) and (24) the values of u, v have been evaluated numerically for $2\omega t = 0, 1, 2, \ldots 10$ and values of $r/a = 1/\lambda$ between 1 and 4. In the case of u the method has been to evaluate

$$\sum_{s=0}^{\infty}(-)^s\lambda^3 f_s(\lambda)\frac{(2\omega t)^{2s}}{2s!}.$$

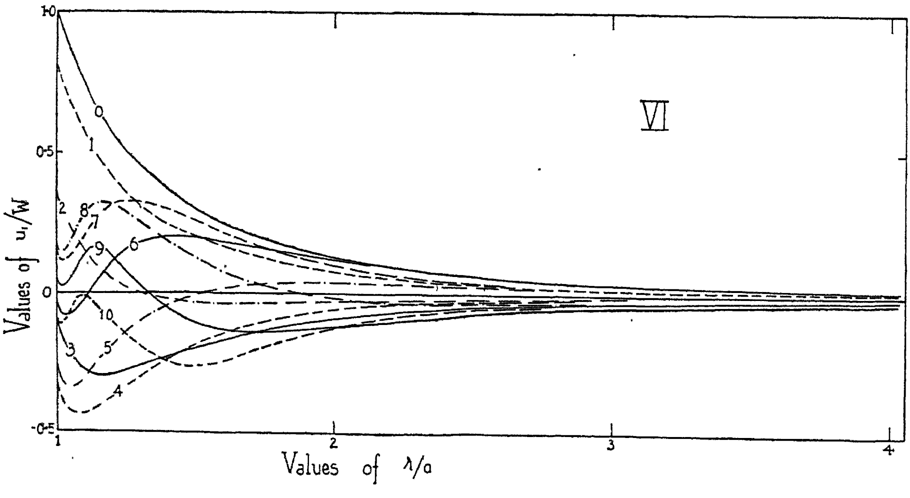
Here it was found necessary to work to eight figures and use was made of an arithmometer. From the results the values of

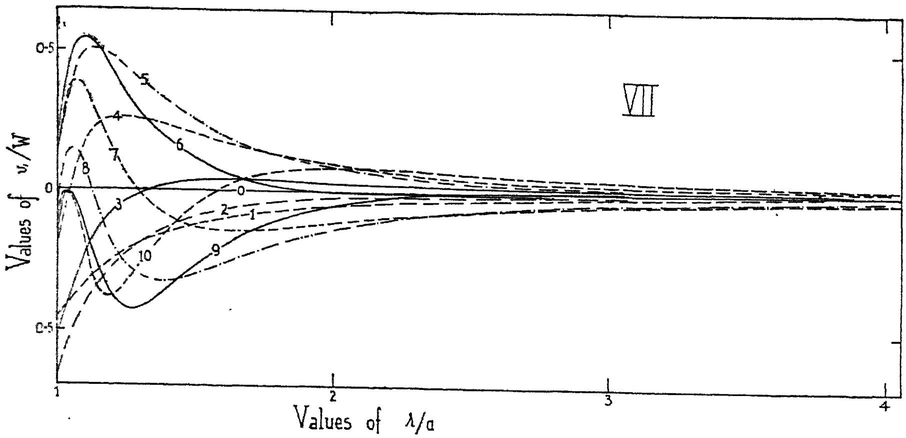
$$\int_0^\lambda \sum_{s=0}^{\infty} (-)^s \lambda^2 f_s(\lambda) \frac{(2\omega t)^{2s}}{2s!} \, d\lambda$$

were obtained by numerical integration. The values of $J_0\{2\omega t\sqrt{(1-\lambda^2)}\}$ were computed from tables and $\int_0^\lambda \lambda^2 . J_0\{2\omega t\sqrt{(1-\lambda^2)}\}\, d\lambda$ obtained by numerical integration.

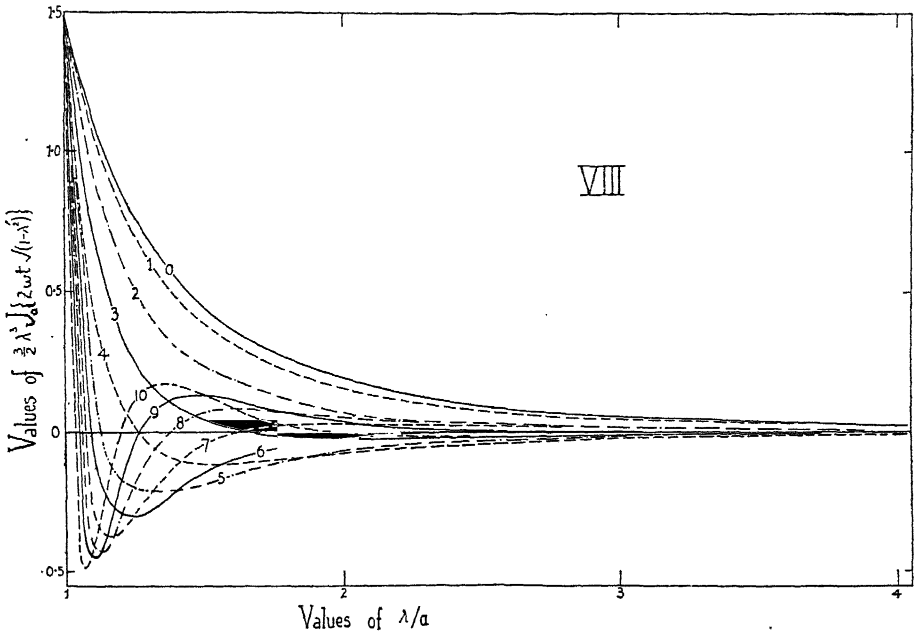
A similar process was adopted to evaluate v.

From the results the Diagrams VI, VII and VIII have been constructed. Diagram VI represents the variation of u_1, the various curves denoting the variation of u_1/W with r/a for $2\omega t = 0, 1, 2, \ldots 10$. Diagram VII denotes





similarly the variation of v_1. Diagram VIII gives the variation of $\frac{3}{2}\lambda^3 \,.\, J_0\{2\omega t\sqrt{(1-\lambda^2)}\}$; this function has the value $1\cdot5$ for $\lambda = 1$ for all t.



The functions u_1, v_1 tend rapidly to zero away from the sphere, indicating that the disturbance of the liquid is practically confined to the immediate neighbourhood of the sphere, but not to such a pronounced degree as in the motion parallel to the axis of rotation. The disturbance at any point attains a maximum value before tending to zero, the time of attaining this maximum increasing with the distance from the centre of the sphere.

Velocity of the Liquid at Points on the Sphere.

§ 10. Expressing the dynamical equations 3 (A) in terms of the spherical polar co-ordinates r, θ, ϕ, we obtain

$$\begin{aligned} &\frac{\partial u'}{\partial t} - 2\omega v' \cos\theta = -\frac{\partial \mathrm{P}}{r\partial\theta}, \\ &\frac{\partial v'}{\partial t} + 2\omega w' \sin\theta + 2\omega u' \cos\theta = -\frac{\partial \mathrm{P}}{r\sin\theta\,\partial\phi}, \qquad (25) \\ &\frac{\partial w'}{\partial t} - 2\omega v' \sin\theta = -\frac{\partial \mathrm{P}}{\partial r}, \end{aligned}$$

and, on the sphere, the radial velocity (w') is given by

$$(w')_{r=a} = \mathrm{U}\sin\theta\cos\phi + \mathrm{V}\sin\theta\sin\phi$$
$$= \tfrac{3}{2}\mathrm{W}\sin\theta\,\{\cos\phi\,\mathrm{S}'_1(2\omega t) - \sin\phi\,\mathrm{S}_1(2\omega t)\}/2\omega t.$$

Now

$$\left(\frac{\partial \mathrm{P}_{2s}}{\partial r}\right)_{r=a} = (-)^s\,\tfrac{3}{2}\mathrm{W}\sin\theta\sin\phi\left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}, \quad s \geqslant 0,$$

$$\left(\frac{\partial \mathrm{P}_{2s-1}}{\partial r}\right)_{r=a} = (-)^{s-1}\,\tfrac{3}{2}\mathrm{W}\sin\theta\cos\phi\left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}, \quad s > 0,$$

and

$$\left(\frac{\partial \mathrm{P}}{\partial r}\right)_{r=a} = 2\omega\sum_{s=0}^{\infty}\left(\frac{\partial \mathrm{P}_s}{\partial r}\right)_{r=a}\frac{(2\omega t)^s}{s!}$$

$$= 2\omega\,\frac{3}{2}\mathrm{W}\sin\theta\sin\phi\sum_{s=0}^{\infty}(-)^s\left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}\frac{(2\omega t)^{2s}}{2s!}$$
$$- 2\omega\,\frac{3}{2}\mathrm{W}\sin\theta\cos\phi\sum_{s=1}^{\infty}(-)^s\left\{\mu^{2s} - \frac{1}{(2s+1)(2s+3)}\right\}\frac{(2\omega t)^{2s-1}}{(2s-1)!}$$

$$= 3\omega\mathrm{W}\sin\theta\,\{\sin\phi\cos(\mu 2\omega t) + \cos\phi\cos\theta\sin(\mu 2\omega t)\}$$
$$+ 3\omega\mathrm{W}\sin\theta\cos\phi\,\{\mathrm{S}'_1(2\omega t) - 2\mathrm{S}_1(2\omega t)/2\omega t\}/(2\omega t)^2$$
$$- 3\omega\mathrm{W}\sin\theta\sin\phi\,.\,\mathrm{S}_1(2\omega t)/(2\omega t)^2,$$

so that

$$(v')_{r=a} = \frac{1}{2\omega\sin\theta}\left(\frac{\partial w'}{\partial t} + \frac{\partial \mathrm{P}}{\partial r}\right)_{r=a}$$

$$= \tfrac{3}{2}\mathrm{W}\sin\phi\left\{\cos(2\omega t\cos\theta) - \frac{\mathrm{S}'_1(2\omega t)}{2\omega t}\right\}$$
$$+ \tfrac{3}{2}\mathrm{W}\cos\phi\left\{\cos\theta\sin(2\omega t\cos\theta) - \frac{\mathrm{S}_1(2\omega t)}{2\omega t}\right\}.$$

Again, on $r = a$,

$$\frac{1}{a\sin\theta}\frac{\partial \mathrm{P}_{2s}}{\partial\phi} = (-)^{s-1}\frac{\tfrac{3}{2}\mathrm{W}\cos\phi}{(2s+1)(2s+3)},$$

$$\frac{1}{a\sin\theta}\frac{\partial \mathrm{P}_{2s-1}}{\partial\phi} = (-)^{s-1}\frac{\tfrac{3}{2}\mathrm{W}\sin\phi}{(2s+1)(2s+3)},$$

hence

$$\left(\frac{\partial \mathrm{P}}{r\sin\theta\,\partial\phi}\right)_{r=a} = -\frac{3\omega\mathrm{W}}{(2\omega t)^2}\left[\cos\phi\,.\,\mathrm{S}_1(2\omega t) + \sin\phi\left\{\mathrm{S}'_1(2\omega t) - \frac{2\mathrm{S}_1(2\omega t)}{2\omega t}\right\}\right],$$

and from (25) we now have

$$(u')_{r=a} = \tfrac{3}{2}\mathrm{W}\sin\phi\left\{\sin(2\omega t\cos\theta) - \cos\theta\,\frac{\mathrm{S}_1(2\omega t)}{2\omega t}\right\}$$
$$- \tfrac{3}{2}\mathrm{W}\cos\phi\cos\theta\left\{\cos(2\omega t\cos\theta) - \frac{\mathrm{S}'_1(2\omega t)}{2\omega t}\right\}.$$

If we graph the functions $(u')_{r=a}$, $(v')_{r=a}$ for a constant value of ϕ, it is found that they exhibit the same general characteristics as are indicated by diagrams V (A) and VI (A). If, however, we denote by u'' and v'' the tangential components of the velocity of the liquid relative to the sphere at points on the sphere, we find that

$$u'' = \tfrac{3}{2}\mathrm{W} \sin \phi \sin (2\omega t \cos \theta) - \tfrac{3}{2}\mathrm{W} \cos \phi \cos \theta \cos (2\omega t \cos \theta),$$

$$v'' = \tfrac{3}{2}\mathrm{W} \sin \phi \cos (2\omega t \cos \theta) + \tfrac{3}{2}\mathrm{W} \cos \phi \cos \theta \sin (2\omega t \cos \theta).$$

Thus u'', v'' are the components, in the tangent plane at a point of the sphere, of a vector through the point which has components $-\frac{3}{2}\mathrm{W} \cos (2\omega t \cos \theta)$ parallel to Ox and $\frac{3}{2}\mathrm{W} \sin (2\omega t \cos \theta)$ parallel to the line obtained by rotating Ox through $\frac{1}{2}\pi$ about the radius vector.

Consequently, at a point on the sphere, the relative velocity of the liquid is the component in the tangent plane of a vector of constant magnitude $\frac{3}{2}\mathrm{W}$; this vector passes through the point of the sphere in question and describes a right circular cone, drawn inwards from the point, with angular velocity $-2\omega \cos \theta$; the axis of the cone is the radius vector through the point and the initial position of the vector is opposite to the direction of projection of the sphere.

It will be noticed on reference to § 9 (A) that this description also applies to the motion in the case of projection parallel to the axis of rotation.

Finally we notice that the components of vorticity tend to become large with time; hence, as in the previous problem, the solution only represents the true state of the liquid for a restricted time.

The Photometric Matching Field.

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Communicated by Prof. H. L. Callendar, F.R.S.

(Received June 1, 1923.)

Part I.

The basis of experimental photometry is the power of the eye to judge the equality of illumination in the parts of a photometric field. It is commonly stated that the parts to be equalised should be uniformly illuminated and should be as far as possible placed in immediate juxtaposition, so that the line of separation tends to disappear when equality is reached. (We do not consider for the present the case of photometers employing the equal contrast principle.) Until comparatively recently, however, it was not fully realised that the minimum contrast which is perceptible depends on several conditions amongst the chief of which are :—

(1) The brightness of the retinal image of the field.
(2) The state of adaptation of the eye.
(3) The portion of the retina employed for visual observation.
(4) The size and shape of the contrasting patches.

The "standard" work on the value of the so-called Fechner fraction* is that of König and Brodhun† who employed a bi-partite field and produced the contrast by a polarisation method. The field was in the form of two superimposed rectangles; the height of each subtended 3° at the eye, while the common breadth was $4\frac{1}{3}°$. Their results have been examined and re-calculated by Nutting,‡ who also examined§ the value of the unit of brightness employed. Blanchard|| also described experimental work bearing on the

* ds/S = "Fechner fraction"; where S is the field brightness which can just be distinguished from a brightness $S+ds$.

† "Psychophysische Fundamentalformel," 'Sitz. Akad. d. W., Berlin' (1888), p. 917.

‡ 'Bull. Bur. Standards, U.S.A.,' vol. 3, p. 59 (1907).

§ 'Trans. Ill. Eng. Soc. (America),' vol. XI, p. 4 (1916).

|| 'Phys. Rev.,' 2nd Series, vol. XI, p. 90 (1918).

same point. Owing to the number of factors concerned, however, the various conditions obtaining in some of the experiments make the results difficult to compare.

The conditions relating to contrast perception are similarly concerned in regard to the "threshold" value of brightness for the beginning of visual stimulation. In this case, at least, it is well known that the size of the stimulus surface exercises a profound influence. The review of the subject given by Parsons* leaves no room for doubt as to the nature of the main facts, but inasmuch as there are certain discrepancies in the details of the results thus described, and between those of Loeser, Druault, Abney and Watson, and Paterson and Dudding, it appeared desirable to the present writer (some years ago) to repeat some of the experiments, more especially with a view to testing the normal threshold effect, in which no effort is made to select any particular portion of the retinal surface for the impression. The results obtained in that year have already been published,† and they indicated (in brief) that, up to an angular subtense of the diameter of the stimulus surface of approximately 1°, the threshold brightness is nearly inversely proportional to the solid angle subtended by the source, and between 1° and 5° the threshold is inversely proportional to the plane angle subtended by its diameter. This agrees with the results of Ricco and Charpentier as described by Parsons. In order that the subject of the present paper may be fully understood a curious effect noticed in these experiments must be recalled.

Previous Results.—The method employed in my investigations involved the use of test objects consisting of round or square discs of black paper of such sizes as to subtend known visual angles. They were mounted on a background screen of black velvet. When illuminated by a divergent beam of light (the intensity of which could be controlled) the appearance presented was that of a large disc of very low brightness with a smaller and brighter central patch. On decreasing the general illumination a point is found at which the smaller disc seems to lose its definite shape and appears as a smaller blur of light; finally it becomes indistinguishable. It was found that the angular subtense of the illuminated background had a large influence on the amount of light necessary to perceive the central disc.

* 'Introduction to the Study of Colour Vision.'

† Department of Scientific and Industrial Research—'Bulletin No. 3' (1919).

The magnitude of the effect is illustrated by the following table :—

Angular subtense of central object disc = 13 minutes.

Subtense of background in degrees.	Relative illumination required to perceive the same disc, *i.e.*, to distinguish it from the background.
11	10
9	16
6·5	17
4	20
3·4	28

In an additional experiment it was arranged that the subtense of the background could be at will suddenly increased from 11° to over 90°; it was found that under suitable conditions an object which could not be distinguished at all from a background of 11° was brought clearly into view solely by thus increasing the background so as to throw light on the peripheral portions of the retina.

Results of other Observers.—A phenomenon (at first sight apparently similar) has been noticed by Nutting* who sensitised his eye with a very large field (of brightness 0·1 milli-lamberts) and then found the brightness of a small white disc necessary to perceive it immediately on "snapping off" the sensitising field. The area of the sensitising field could be varied, and it was found that the threshold brightness was considerably raised when the area of this field was reduced. The conditions of the experiment were, however, essentially different from those adopted by the present writer and described above.

Blanchard† describes similar work in which the brightness of the central contrast field (taking the place of Nutting's plain disc) is varied, and the relation between this brightness and the minimum perceptible contrast is found. L. A. Jones‡ refers to this work and gives curves which are stated to show how the minimum perceptible contrast depends on the *adaptation level of the retina.* These results were obtained with Nutting's visual sensitometer, but it is not made clear how the "adaptation level" (presumably controlled by the large sensitizing field) was related to the brightness of the central contrast field. It is clear, however, from the results of König and Brodhun, and of Blanchard, that the discriminating power of the eye for

* *Loc. cit.*, p. 1.

† 'Phys. Rev.,' vol. XI, No. 2, p. 81 (1918).

‡ 'Trans. Ill. Eng. Soc. (America),' Oct., 1920, and other papers.

contrast becomes greatest at a *medium* field brightness when the field is of fair angular extent. Jones found that a better result can be secured in observing kinematograph pictures if the surroundings of the screen are not entirely dark, and he attributes this to the "raising of the adaptation level."

Karrer and Tyndall* have described an investigation on the contrast sensibility of the eye, which is more directly comparable with my own work. They noted that if during an observation a peripheral portion of the retina was accidentally illuminated by an auxiliary screen to one side of the line of vision, the contrast to be observed became more visible.

Reeves† has described work on the effect of size of stimulus on the contrast sensibility of the retina, in which an attempt is made to secure a complete standardisation of conditions. Apparatus similar to that described by Nutting was employed, and observations were taken on a fixed contrast made by placing a strip of neutral gelatine over a part of the white disc employed as

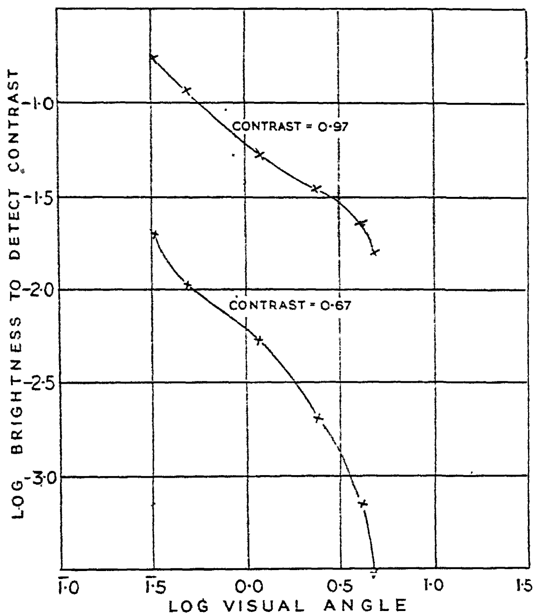


Fig. 1.

a test object. The eye was first adapted to the brightness of the sensitising field, which was then snapped off, and the brightness of the disc necessary to ensure that the contrast shall be perceptible after a definite period of dark adaptation was found. It is interesting to take Reeves's results for contrasts

* "Scientific Papers," 'Bureau of Standards,' Washington, No. 366.

† 'Jour. Opt. Soc. Amer.,' vol. I, Nos. 5 and 6.

of $0 \cdot \dot{6}7$ and $0 \cdot 97$ (results obtained after 60 seconds dark adaptation) and plot (see fig. 1) logarithms of the brightness required to see the contrast, against logarithms of the visual angle subtended by the stimulus surface. It is at once seen that at a subtense of the surface of about 1° the light required to view the contrast is roughly inversely proportional to the angular subtense, but between 3° and 5° it is inversely proportional to the square or cube of this amount.

Although it is not expressly stated in Reeves's paper, the results seem to indicate that he used central fixation to observe the contrast patch, and thus his results indicate the effect of including parts of the macula further and further from the fovea as the angular subtense of the patch increases. The rod-free area subtends at an angle on the visual field of about 3° and the most sensitive portion is reached (according to Abney and Watson) at 5° from the fovea centralis.

In ordinary photometry, general unrestricted eyesight uses peripheral and central regions of the retina at will; this perhaps explains the apparent discrepancy between the results of Reeves and those of other observers. With unrestricted vision, the light required to view a fixed contrast is inversely proportional to the angular diameter of the stimulus at all points between 1° and about 5° (at least under the special and somewhat different conditions employed by the present writer). The above considerations would appear to limit the use of Reeves's results for ordinary problems of contrast visibility. Nevertheless, these results definitely point to the decided advantage in photometric sensibility which accrues from an increase of the visual angle of the field, especially when a low general brightness has to be employed.

Nutting* states that "the size of the photometric field is of little consequence, but it may properly be limited to about $4\frac{1}{2}$°." It seems probable that in the light of the results which have been described, this conclusion hardly does justice to our present knowledge. The general indication is, apparently, that maximum sensitiveness in the presence of a brightness contrast necessitates having both parts of the field of view exceeding a certain minimum angular subtense, and *also* on the working of as large as possible an extent of the retina at a fairly uniform level of brightness. *The second part of the present paper deals with a method of securing the latter condition and thus increasing the accuracy of photometric measurements.*

Suggested Explanations.—It may be of interest, however, to recall some of the suggestions which have been offered to explain certain of the foregoing

* 'Outlines of Applied Optics.'

phenomena. Abney* noticed that a patch of diminishing luminosity disappears almost as a point, and offered the suggestion that the visual impression is "radiated in all directions over the surface of the retina." In the case of a small patch of low luminosity the brightness would tend to appear greatest at the central point. J. W. French† quotes the theory of Helmholtz‡ that the retina is overlaid by a network of inter-connected nerve fibres; this network is connected on the one side to the sensitive elements of the retina, and on the other side to the *apparently less numerous fibres* of the optic nerve. French thinks that the finest elementary nerve fibres may be much more numerous than is usually supposed, but Helmholtz's theory would accord well with that of Abney. S. D. Chalmers§ gave an interesting electrical analogy by which he explained results similar to those obtained by the writer on the threshold phenomena. Certain limited numbers of the retinal elements, he considered, could act in series; if a greater number were brought into action "parallel" grouping was introduced. This again accords fairly well with the ideas of Helmholtz.

Ferree, in discussing Nutting's experiments,|| observed that effects on similar lines have been described by Purkinje, Brucke, and others. The phenomena observed by Nutting were considered to be due to the after-effects of physiological induction. The pre-exposure field was thus made subjectively brighter by the presence of surrounding darkness, *and the effect was the greater when the subtense of this field was reduced.* The dark after-image tended to suppress the response of the eye to the centre spot.

To this explanation it might be objected that it has been often observed (as by Abney) that a small bright field is apparently less luminous than a larger one which is really equal in intrinsic luminosity; this hardly agrees with one of the statements made by Ferree. It is perfectly true that a dark after-image is a suppression of the response of some portion of the retino-cerebral receiving apparatus, but the change in the effect with varying angle of field does not seem to be adequately explained if Abney's observation is correct.

As was previously mentioned, L. A. Jones suggests that, when the peripheral regions of the retina are illuminated, the adaptation level of the retina is

* 'Researches in Colour Vision,' p. 178.
† 'Trans. Opt. Soc.,' vol. XXI, p. 139.
‡ 'Handbuch der Physiologischen Optik.'
§ 'Trans. Opt. Soc.,' vol. XX, p. 303.
|| *Loc. cit.*, p. 1.

raised; he thus attempts to explain the increase of sensibility on the basis of the results of König and Blanchard, viz., the greater discriminating power of the eye for contrast when passing from fields of very low brightness to those of average (daylight) brightness. If the "adaptation level" were really raised then the "threshold" should be raised. Nutting's work showed clearly enough, however, that the threshold was lowered when the peripheral portions of the retina were light adapted. We must, therefore, conclude that Jones's supposition is incorrect.

To sum up, there seems no doubt that the interconnection of retinal elements as suggested by Helmholtz offers the most probable start for an explanation. The series grouping might be considered to be non-existent in the fovea, but to be valid over visual angles of the order of one degree square somewhat away from this region. It appears somewhat cumbersome to consider that another type of grouping comes sometimes into action, for the mind is led to wonder, on the electrical analogy, how the "changes in connection" are effected. Another suggestion may perhaps be made, namely that the passage of an impulse along a fibre of the optic nerve tends to sensitise sympathetically the fibres in its vicinity and makes them more responsive to slight impulses. Or, alternatively, such a relative sensitisation might produce a greater response to slight changes of intensity.

An interesting experiment which illustrates very well the supposed effect of interconnection may be made as follows:—Place on a dark wall a piece of white paper subtending about 2° or 3° square at the eye. Direct the gaze fixedly to a second point above it and about 30° from the centre of the paper. If the paper is not too bright it will then usually disappear in a few seconds. Any disc larger than about 2° or 3° will, however, remain visible much longer at least. The disappearance cannot be attributed to retinal fatigue, and can hardly be due to any structural incapacity of the retino-cerebral transmitting, conducting and receiving apparatus, for, if the direction of gaze be shifted slightly further away from the paper, the latter is temporarily clearly seen and its shape likewise. It would possibly be explained by the failure of the brain correctly to sort out the impulses arriving by differing nerve routes unless there is a sudden change in these sufficient to cause a momentary "attention."

The supposed "interconnection" of retinal elements separated by an amount corresponding to more than about 1° in the visual field might thus be explained on the basis of the imperfect discriminating power of the brain, and its tendency to integrate visual impressions when these are not sufficiently

definite to be assigned to specific locations in the same image, bearing in mind also the possibility of sympathetic sensitisation of the optic nerve fibres adjacent to one along which an impulse is passing.

Part II.—A Device for Increasing the Accuracy of Settings in Photometric Instruments.

The phenomena noted in Part I of the present paper suggest a possible means of improving the field of view in a photometer. Let B and C (fig. 2) be the contrasting halves of a simple field. Their combined breadths are usually, by optical means, made to subtend an apparent angle of 1° to 4° at the eye, and it is usually the case that further optical magnification is not convenient. If the illumination of the peripheral portions of the retina increases the contrast sensitiveness of the central portions, it would appear that some

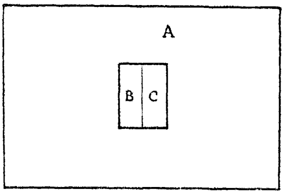


Fig. 2.

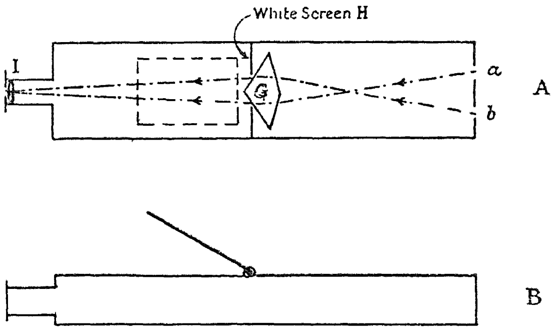


Fig. 3.

increase in accuracy should be obtained simply by surrounding the matching field by a field of approximately the same (though not necessarily identical) brightness. In many instruments this can be done without much structural alteration, though care is necessary in avoiding stray light.

Preliminary Experiment.—Figure 3 exhibits in plan and side elevation the apparatus employed for some preliminary experiments to test the above idea. A shallow rectangular box has rectangular apertures at *a* and *b*. The glass rhomb G is situated just behind a rectangular opening in the screen H which extends across the box. The eye views the separating edge of the rhomb with the aid of a lens I; the angles of the rhomb are so arranged that the right hand side of the field is illuminated by light from *a*, and the left hand by light from *b*. The side of the screen H nearest the eye is white and is illuminated by a window in the top of the box, the opening and closing of which suffices

to adjust the value of the brightness sufficiently nearly to that of the central field, or entirely to cut off the light from the outer field.

For a commencement, tests were made by holding some of the Tintometer Company's glass slips of low scale value before one or other of the apertures when these were both illuminated by light diffusely reflected from matt porcelain. It was agreed by several observers that the conditions for observation seemed to be improved, but that a more systematic test was required. A beam from a Pointolite lamp was passed through a "neutral" photometer wedge and thus to a piece of opal glass held against the aperture a, while b was illuminated by a non-variable beam from the same lamp. The intensity of the second beam could be reduced, as required, by filters, and a series of matches could then be made by the wedge.

The procedure adopted was to make five settings at a time; the first five with a dark surround for the central field, the second five with a bright surround, and so on. Each observer took 15 to 20 settings with both light and dark conditions. No rejection of bad results was allowed in numerical reduction, which was carried out by the method which will be clear from the table below. The dimensions were :—

Central field 1·3° wide by 1·4° high (approximately).
Outer „ 17° „ „ 3·5° „ „

The brightness of the field employed in the tests was of the order of 20–50 milli-lamberts.

The readings on the scale of the photometer wedge were read and noted by a separate person in every case, so that the observer had no idea of the numerical readings he was making.

Observer H.

Dark outer field.		Light outer field.	
Wedge reading.	Difference from the mean of the five results in same group.	Wedge reading.	Difference from the mean.
37·8	−0·4	37·9	−0·7
36·8	−1·4	39·1	+0·5
39·1	+0·9	37·9	−0·7
37·9	−0·3	39·5	+0·9
39·3	+1·1	38·7	+0·1

Observer H then continued, and took 15 readings with both light and dark outer field; other observers followed suit. Treating the above differences

as "errors," the Mean Error (*i.e.*, the square root of the mean of the squares of such "errors") proved to be :—

	Mean error.	
	Dark outer field.	Light outer field.
Observer H	0·750	0·624
,, P	1·55	0·83
,, C	2·57	1·43
,, L	1·81	0·81

These observers were students with no previous experience of photometric work; their lack of training is reflected in the large divergences of the mean error. Their results give, however, decisive evidence of the improvement in the precision of setting when the bright surround to the field is employed, even though this is not precisely of the same brightness as the central matching field.

Experiments with Fresh Apparatus.—The Nutting Spectrophotometer attachment to the Hilger Wave-Length Spectrometer offered a ready means for further testing the effect. As it was not desired to use coloured light at the present stage the dispersing prism was replaced by a simple 90° periscope prism and the field was thus colourless. A piece of neutral glass was placed in one beam, when a match could be made by rotating the circle of the photometer. The eyepiece employed is suggested in fig. 4. The matching field

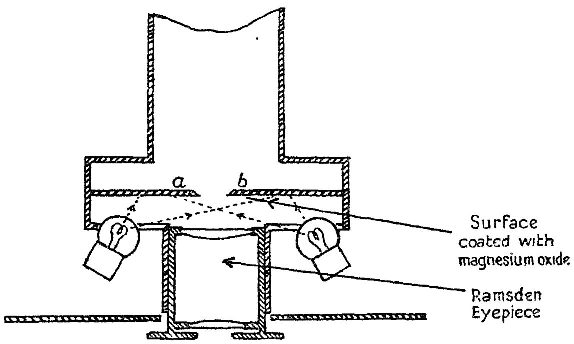


FIG. 4.

appears between the jaws *a* and *b* of an adjustable slit. These jaws were coated on the side nearest the eyepiece with magnesium oxide from the smoke of burning magnesium ribbon (which gives a uniform and almost perfect diffusing surface), and they could be illuminated by light from a small 4-volt lamp

(run in series with a variable resistance) placed to one side of the eyepiece and suitably shaded from the eye. A Gauss eyepiece was first tried, but the back reflected images interfered too much with the matching field. When the arrangement is properly made the original matching field appears in the centre of a much larger bright field, the relative dimensions being :—

Width of central tripartite field $= 2\frac{1}{2}°$ (approximately).
Width of outer field $= 20°$,,

The general brightness of the outer field could be found in any condition, with the aid of a Holophane Lumeter and the Nutting Photometer, by moving the photometer circle till the brightness of the field matched that of a screen standing behind the instrument ; the screen could be examined with the Lumeter and the original brightness of the photometer field could then be calculated. Suitable variations in brightness were obtained by the use of filters in one or both beams.

Three observers, A, B and C, made experiments with this apparatus, the procedure being very similar to that previously carried out : Sets of five settings were made with light and dark outer fields alternately, and readings were taken on the density scale. Results were as given in Table on next page.

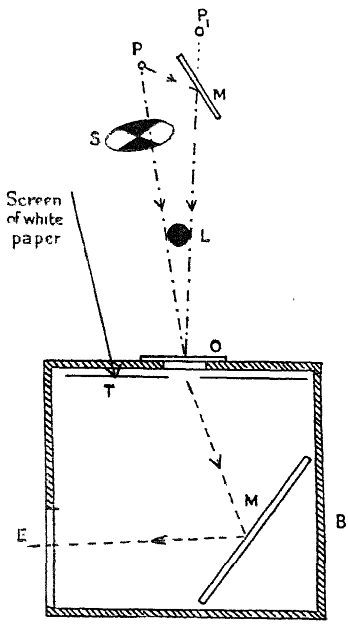


FIG. 5.

The Contrast Limen.—The increase of precision suggested by the foregoing results indicated the desirability of testing the extent to which the contrast "limen" (or least perceptible difference of intensity between the parts of a matching field) can be diminished (if at all) by using a bright surrounding field. For this test a shadow photometer of very simple description was employed (fig. 5). P is a Pointolite lamp and P_1 its image formed in a mirror M of platinised glass. S is a variable sector which could be controlled by the observer whose head is at E and who views the field with both eyes. The rod L and the piece of opal glass O form a shadow photometer, the contrast being seen from behind the screen with the aid of the mirror M. T is a screen of white paper which can be illuminated when necessary by a small 4-volt lamp

in the upper part of the box B. The whole makes a convenient arrangement for testing the precision of photometric settings under the conditions required. The angular subtense of the central circular bright field was 4°, and that of the surrounding rectangular bright field was 18° × 26°. The approximate brightness of the field employed was fairly low, *i.e.*, 0·16 milli-lamberts.

Brightness of field (milli-lamberts).		Mean error (density scale).	
		Light outer field.	Dark outer field.
Observer A	12·2	0·007	0·0145
,, B	15·8	0·013	0·019
,, C	1000·0	0·0107	0·0140

Sector Readings with Shadow Photometer, using Light and Dark "Surround" to the Contrast Field.

(The Sets 1, 2, 3 and 4 were taken in succession with no rest.)

Set A.

(1) Dark Surround.				(2) Light Surround.			
Left just darker.	E.*	Right just darker.	E.	Left just darker.	E.	Right just darker.	E.
30·1	+0·7	26·7	−0·2	29·2	+0·2	27·1	+0·0
29·2	−0·2	26·3	−0·6	29·0	0·0	27·7	+0·6
29·4	0·0	26·8	−0·1	29·0	0·0	26·8	−0·3
29·1	−0·3	27·1	+0·2	28·8	−0·2	27·0	−0·1
29·2	−0·2	27·5	+0·6	29·2	+0·2	27·0	−0·1

Means :—29·4 ....26·9
Difference (= 2 Limen) = 2·5
Limen = 4·5 per cent..

Means :—29·0 ....27·1
Difference (= 2 Limen) = 1·9
Limen = 3·4 per cent.

(3) Dark Surround.				(4) Light Surround.			
Left just darker.	E.	Right just darker.	E.	Left just darker.	E.	Right just darker.	E.
28·5	−0·4	26·9	+0·3	29·2	−0·4	26·9	0·0
28·9	0·0	27·1	+0·5	29·4	−0·2	27·2	+0·3
27·6	−1·3	27·0	+0·4	29·7	+0·1	27·3	+0·4
30·2	+1 3	26·8	+0·2	29·8	+0·2	26·2	−0·7
29·3	+0·4	25·2	−1·4	29·8	+0·2	27·0	+0·1

Means :—28·9 ....26·6
Difference (= 2 Limen) = 2·3
Limen = 4·1 per cent.

Means :—29·6 ....26·9
Difference (= 2 Limen) = 2·7
Limen = 5 per cent.

Set B.

(1) Light surround.				(2) Dark surround.			
Left just darker.	E.	Right just darker.	E.	Left just darker.	E.	Right just darker.	E.
39·2	0·0	36·9	0·0	40·2	+0·5	37·8	+1·2
39·8	+0·6	37·9	1·0	39·3	−0·4	35·8	−0·8
38·9	−0·3	37·0	0·1	40·1	+0·4	36·3	−0·3
39·2	0·0	35·9	−1·0	39·0	−0·7	35·9	−0·7
38·9	−0·3	36·6	+0·3	40·1	−0·4	37·2	+0·6

Means :—39·2 ....36·9
Difference (= 2 Limen) = 2·3
Limen = 3 per cent.

Means :—39·7 ....36·6
Difference (= 2 Limen) = 3·1
Limen = 4 per cent.

(3) Light surround.				(4) Dark surround.			
Left just darker.	E.	Right just darker.	E.	Left just darker.	E.	Right just darker.	E.
39·9	−0·2	37·6	+0·2	38·8	−0·5	36·4	+0·8
40·5	+0·4	37·3	−0·1	38·8	−0·5	33·8	−1·8
41·0	+0·9	37·6	+0·2	39·2	−0·1	35·5	−0·1
39·8	−0·3	37·2	−0·2	39·8	+0·5	35·1	−0·5
39·4	−0·7	37·2	−0·2	39·9	+0·6	37·0	+1·4

Means :—40·1 ....37·4
Difference (= 2 Limen) = 2·7
Limen = 3·5 per cent.

Means :—39·3 ....35·6
Difference (= 2 Limen) = 3·7
Limen = 5 per cent.

* The Column E gives the difference from the mean of the five readings.

In considering the foregoing tables, it must be remembered that no rejection of results has been allowed, and that the results will, therefore, differ from those of experiments designed to give the most likely value of the very minimum of detectable contrast. The foregoing investigations will relate more directly to working conditions in the use of photometric instruments. We are probably justified in rejecting the values of the limen given by Section 4 in each of Sets A and B, owing to visual strain, and taking the remaining sections, giving three values of the limen in each case, as more trustworthy. The final results thus are :—

Mean contrast limen with dark surround to matching field = 4·2 per cent.
,, ,, ,, light ,, ,, ,, = 3·3 per cent.

König and Brodhun's table, as interpreted by Nutting, gives a difference limen of 3·5 per cent. under conditions of brightness near those employed in the present work.

The mean errors work out to :—

	Set A.	Set B.
Mean error with light surrounding field	0·29	0·47
,, ,, dark ,, ,, ...	0·62	0·76

In taking Set B the observer was suffering from slight physical indisposition, and this is clearly marked in the lower precision of the results obtained.

To summarize the results obtained, it may be regarded as established that a considerable reduction of the contrast limen can be obtained by stimulating to an *approximately* equal extent the parts of the retina surrounding the portion on which the contrast is to be observed. It is not in any way pretended that the foregoing preliminary experiments are an adequate investigation of the phenomenon. An attempt is now to be made to attack the problem in a much more methodical way, since the result is of considerable importance both from the point of view of photometry and also in connection with the psychological and physiological study of the mechanism of vision. It will not be found difficult to provide means for providing a wider extended field with auxiliary illumination in most types of instruments making use of photometric settings. It may thus be possible to effect a considerable improvement in the precision of saccharimeters, and, in fact, any instrument in which a photometric match is the basis of the indication.

The effect may possibly be found to throw light on the mechanism of colour vision. It will be of interest, for example, to test whether a reduction of the contrast limen occurs when the central field is illuminated by one of the trichromatic primaries and the surround by another primary. These and several other questions, clearly of some interest, remain for investigation.

In conclusion my thanks are due to Mr. O. G. Hay, research student in the Optical Engineering Department, who undertook some of the experiments ; also to Prof. F. J. Cheshire, C.B.E., for his interest and advice. I have also to thank Prof. H. L. Callendar, F.R.S., for reading and communicating the paper.

The Effect of Quenching from above the Carbide Transition Temperature upon the Magnetism of Steel.

By A. A. Dee, B.Sc., D.I.C., Lecturer on Physics, University of Birmingham.

(Communicated by Prof. S. W. J. Smith, F.R.S. Received June 6, 1923.)

1. The transformation which takes place in iron carbide at about 210° C. is best investigated by a study of the thermo-magnetic properties of carbon steel. For among the various changes in the physical properties of the carbide which occur as it is heated through its critical temperature, the loss of the ferromagnetic property is the most outstanding.

Recently it has been suggested by Thompson and Whitehead* that the sudden cooling from about 300° C. of a specimen of carbon steel leads to the suppression of the carbide change. They base their conclusions upon measurements of electrical resistance† and on the difference in the etching properties of the carbide in slowly and quickly cooled specimens. If such is the case, it would appear that low temperature quenching should materially alter the magnetic properties of carbon steels. At the request of Prof. S. W. J. Smith I have tested this inference.

2. A rod of annealed carbon steel ($C = 1 \cdot 1$ per cent.) of length 20 cms. and diameter 5 mms. was selected for examination. The first experiment consisted simply of a determination of the initial part of the I and H curve (*a*) after the specimen had been cooled slowly; (*b*) after the specimen had been quenched from 300° C. in ice-cold water. A magnetometric method was used, and as the experiments were purely comparative the readings of the magnetometer are not reduced to absolute measure. A current of 1 ampere in the magnetising solenoid corresponds to a field of 9 C.G.S. units. The results are shown in fig. 1. The dots represent the observations after quenching and the crosses those after slow cooling. The effect of quenching is almost inappreciable. In further experiments both on this rod and another, the difference between the two cases was always less than 1 per cent., and as it was sometimes one way and sometimes the other it can be set down to experimental error. It would appear, therefore, that quenching from 300° C. has only the feeblest effect on the magnetic qualities of the carbide, and in these circumstances it is difficult

* 'Trans. Faraday Soc.,' May, 1923.

† 'Roy. Soc. Proc.,' A, Feb., 1923.

to believe that the transformation from the non-magnetic to the magnetic form has been suppressed.

3. This view is confirmed by the next experiment, which deals with the effect of heating upon the residual magnetism of the same rod. It was placed

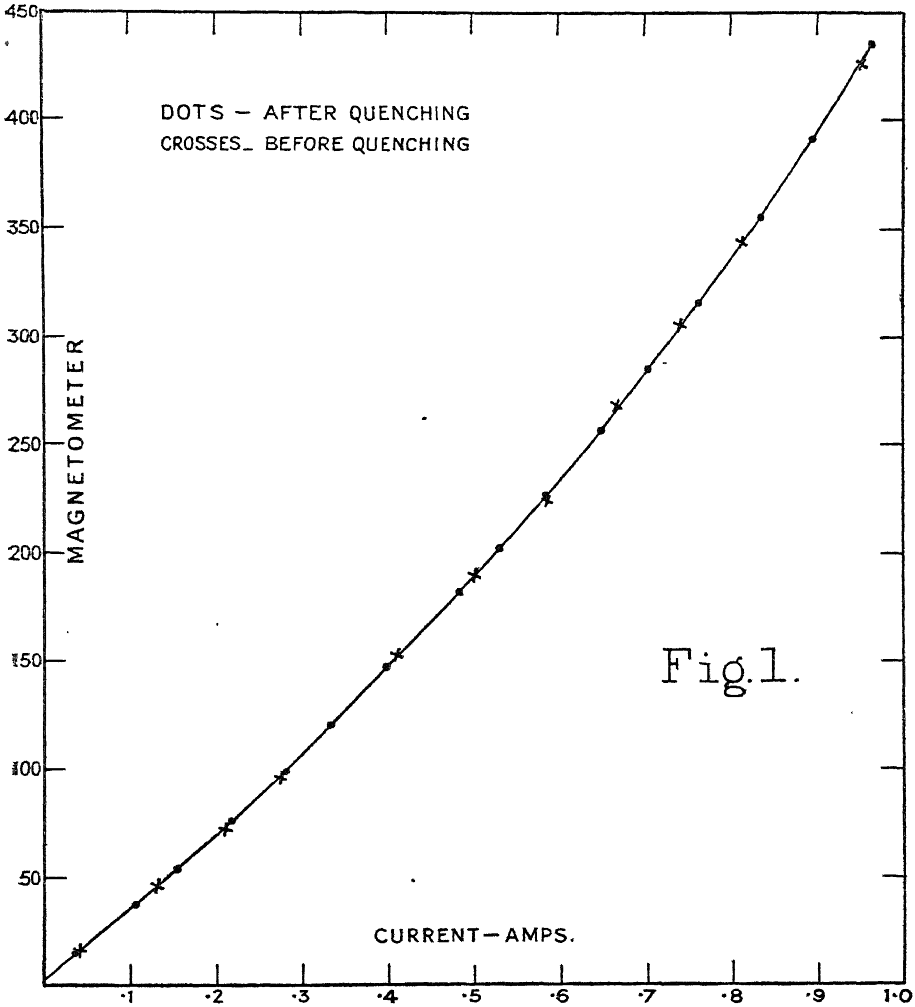


Fig. 1.

in the central tube of a long horizontal bifilarly wound electric furnace, provided with a water-cooled jacket. Over the jacket was wound a magnetising solenoid. The furnace was arranged in the broadside-on position relative to a magnetometer. The rod was magnetised in such a field that on its removal the residual moment gave a suitable deflection to the magnetometer. The variation of this

residual magnetism was observed as the temperature was raised up to about 260° C. As before, the rod was examined after an initial slow cooling and again after quenching from 300° C. The results are shown in fig. 2. The dots

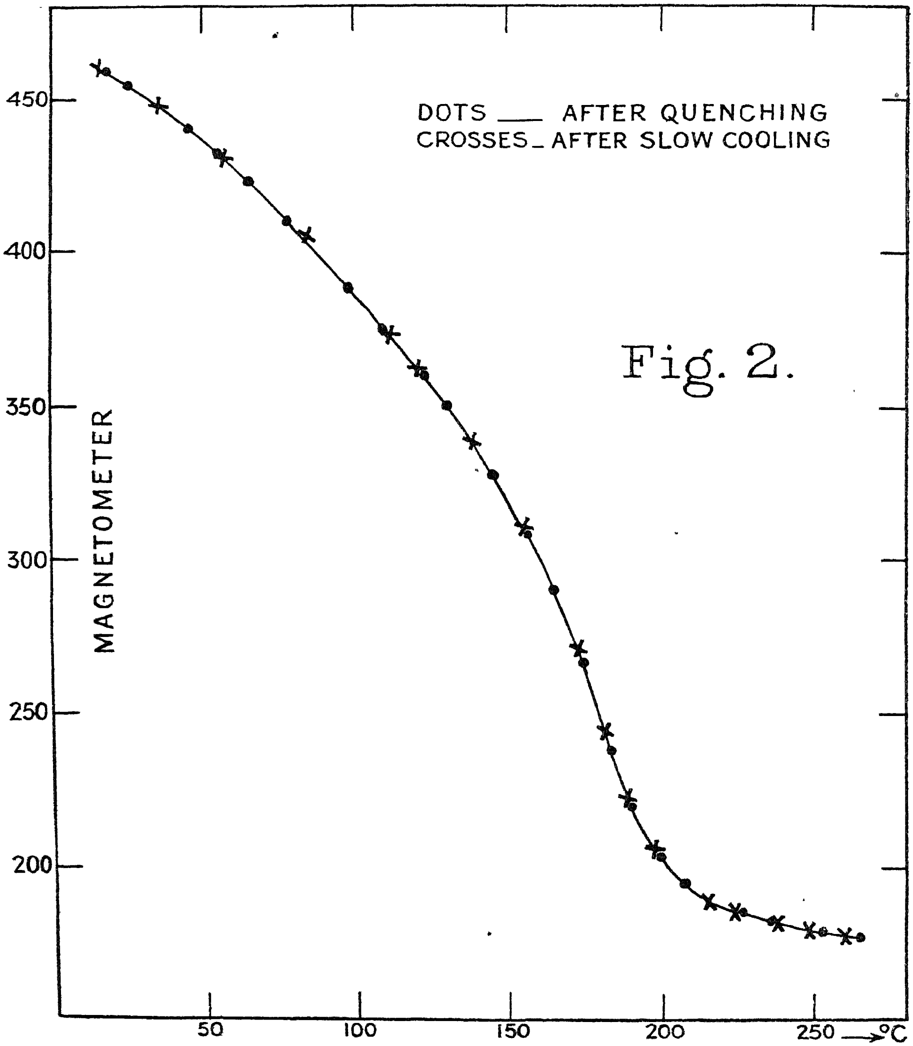


Fig. 2.

represent the observations after quenching and the crosses those after slow cooling. It will be observed that the two curves almost exactly coincide.

The relatively sharp fall in magnetism as the temperature approaches 210° C. is clearly intimately associated with the transition of the carbide. Similar curves for rods of pure iron show no such marked changes in this region of temperature. If, then, the magnetic transformation of the cementite were

suppressed by quenching, the residual magnetism of the rod at air temperature would contain no component due to carbide and in consequence the shapes of the curves near 210° C. should be very different in the two cases.

Again, then, we must conclude that quenching has not suppressed the transformation.

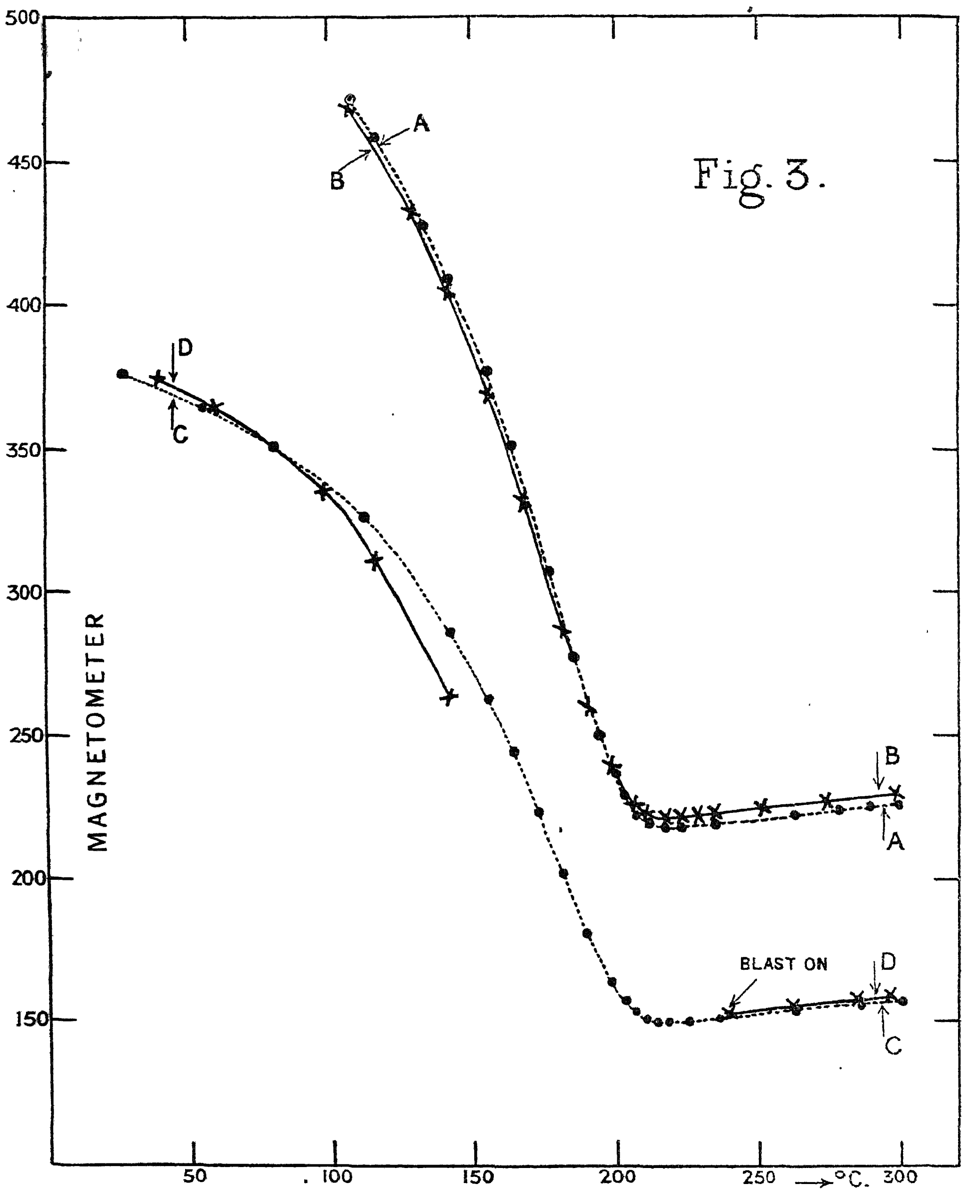
4. The next experiment was as follows. The rod was heated to 300° C. and put through a demagnetising cycle. A field of 4·1 C.G.S. units was then applied and with the field continuously acting the specimen was slowly cooled, the temperature and the magnetometer being observed at intervals. The result is shown in curve A, fig. 3. The relatively rapid augmentation of magnetism which takes below 210° C. is clearly associated with the transformation of the cementite. In fact the minimum point of the curve at 214° C. practically coincides with the transition temperature obtained by the method described by S. W. J. Smith.* It is not, of course, suggested that all the increase in magnetism below 210° is due to the cementite becoming magnetic. There is, in fact, evidence to show that the larger part of this increase is due to iron, but the point to be stressed is that this increment clearly is related to the transformation of the cementite.

5. Thompson and Whitehead suggest that even such a relatively slow cooling as 200° C. in 20 minutes will suppress the cementite change. The above experiment was therefore repeated, only in this case the heating current was switched off at 300° C. in order to get the maximum rate of cooling. In the first case the rod cooled from 270° to 170° C. in one hour and in the second case it cooled over the same range in eight minutes. Curve B shows the quick cooling. Again there is no marked difference between the two cases.

It was thought that a quicker cooling still might possibly lead to some distinct difference. So the above experiments were repeated, only in a lower field of 3·2 C.G.S. units, so that the final deflection at air temperature might be on the scale. But the quick cooling experiment was hurried by directing a blast of air through the tube of the furnace. The blast was started at 240° C., the specimen cooling to 140° in three minutes and down to approximately air temperature after a further six minutes. The result of the slow cooling is shown in curve C, fig. 3, and of the fast cooling in the two parts of curve D. After the blast had been on for a short time observations were recommenced at 140° C. As, however, the thermocouple was attached to the outside of the specimen, it is not until air temperature is approached, and the temperature lag between the couple and the specimen has disappeared, that the readings

* 'Proc. Phys. Soc.,' vol. 25, Pt. 1, p. 78 (1912).

have any value. Again it will be observed that at the lower temperatures there is very little difference between the slowly cooled and the quickly cooled



cases. Therefore we must conclude that the carbide transformation has not been suppressed.

6. If, then, we can take the magnetic properties of cementite as a criterion

of its transformation it would appear that rapid cooling does not retard it to an appreciable extent. The explanation of the results obtained by Thompson and Whitehead must therefore be sought in other directions.

7. By courtesy of Mr. W. V. Mayneord, M.Sc., Research Student in the Physics Department, I am able to include the following evidence obtained by him, corroborating the results shown in fig. 1. His experiments were made by the ballistic method upon a small ring of an annealed carbon steel containing 1·5 per cent. carbon. The permeability was first measured at room temperature (particular care being taken with respect to demagnetisation) for a range of field intensities. The ring was subsequently heated in an electric furnace to 290° C. and quenched suddenly in ice-cold water. The permeabilities were now re-determined at room temperature.

The results, approximately in C.G.S. units, are shown in fig. 4. It will be

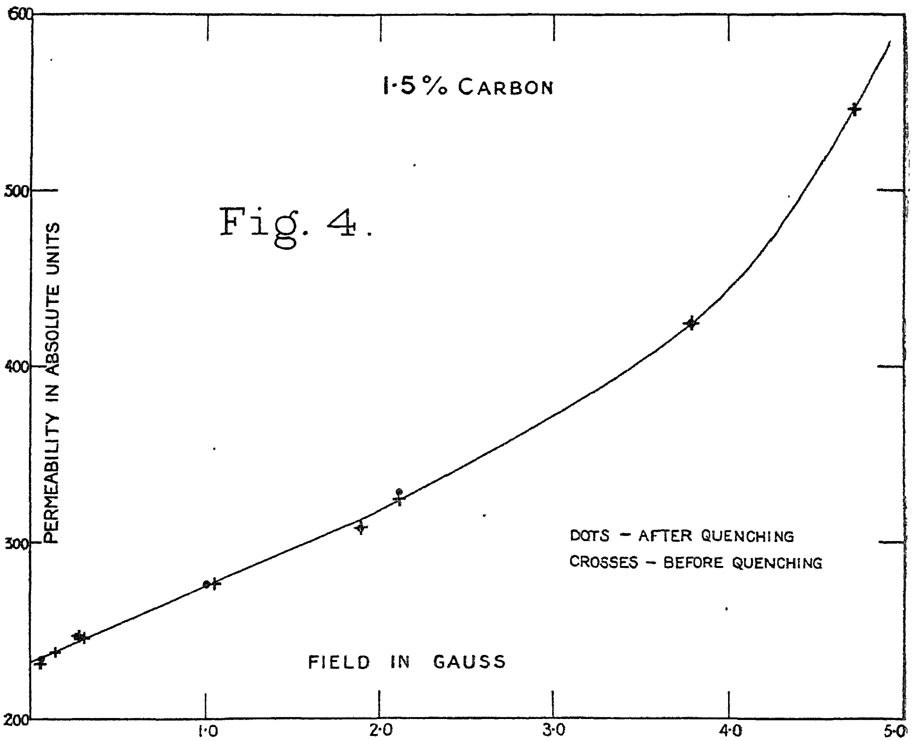


Fig. 4.

seen that quenching produces no appreciable effect upon the permeability in a given field. Similar results were obtained on examining the material 24 hours after the quenching took place. In this case, therefore, as in the first, there is no evidence of any suppression of the magnetic transformation of the carbide resulting from sudden cooling from above the transition temperature.

Further Studies on the Glow of Phosphorus, and its Extinction by Moist Oxygen.

By Lord RAYLEIGH, F.R.S.

(Received August 16, 1923.)

(PLATE 26.)

§1. *Introduction. Blochs' Experiment.*

It has long been known that phosphorus does not glow in moist oxygen at atmospheric pressure and at the ordinary temperature, though, if the oxygen is rarefied or diluted with nitrogen, the glow at once sets in. This has rightly been considered a striking and indeed paradoxical fact. From the point of view of kinetic theory, it seems very strange that collisions between oxygen and phosphorus molecules should never produce chemical action unless their frequency of occurrence in the unit of volume is *below* a certain maximum.

It is believed that the experiments here described will be found at any rate to throw some light on the subject.

The work began with a repetition of the important experiments of L. and E. Bloch.* They found that if a blast of air was allowed to pass over fragments of phosphorus contained in a glass tube, the luminosity could be detached or blown off from the surface of the phosphorus, only making its appearance some way downstream. A dark interval, often of considerable length, separated the phosphorus itself from the luminous cloud. They established further that the production of gaseous ions occurs only in the luminous cloud, and not at the phosphorus surface or in the dark interval.

These phenomena they interpreted by supposing that the oxidation occurs in two stages, phosphorus trioxide being found in the dark interval, and further oxidation to pentoxide in the luminous cloud. Some correspondents of my own have also been attracted to this idea of the oxidation in two stages, but whether it occurs or not I have not, personally, found it helpful in interpreting the luminous phenomena of phosphorescent combustion.

I repeated Blochs' experiment without difficulty in January, 1914, and an observation of some interest was then made. It is known that certain vapours inhibit the oxidation of phosphorus, and that phosphorus cannot be used for the absorption of oxygen in gas analysis if these vapours are present.†

* 'Comptes Rendus,' vol. 147, p. 842 (1908).

† I have examined and in part explained this effect in 'Roy. Soc. Proc.,' A, vol. 99, p. 372 (1921).

In the present case, carbon disulphide was used. A piece of cotton wool moistened with this liquid was tied to the end of a rod, and pushed into the exit end of the large glass tube used in Blochs' experiment. The vapour had no particular effect when the sponge was in the luminous cloud. It was only when the sponge was pushed further upstream so as to be in the dark interval that the inhibiting effect was shown, and the glow ceased. It was not necessary to push the sponge as far as the phosphorus. All that was necessary was that it should be upstream of the luminosity. It may be near the downstream limit of the dark interval, and thus in a position where it could not hinder the supposed formation of trioxide.

This experiment is difficult to reconcile with the theory which explains the dark interval by oxidation in two stages. Since it is observed that in the presence of an inhibitor volumetric absorption of oxygen does not occur, we should have to assume that it is the *first* oxidation to trioxide that is inhibited: for this oxidation, even if it occurred alone without the second stage, would cause absorption of oxygen. On the other hand, in the experiment just described the glow is stopped under conditions where the supposed first stage of oxidation could not be affected. We might, indeed, escape the dilemma by assuming that the inhibiting substance prevents the oxidation to trioxide *and would also prevent* the further oxidation of the latter, if formed, to pentoxide. But this seems improbable, for such inhibition is a very peculiar effect, and does not seem likely to act in the same way on two quite different reactions.

§2. *Improved Method of Experimenting.*

Returning to the subject some years later, I found great difficulty and uncertainty in blowing the luminosity away from the phosphorus.

Since the earlier experiments had been carried out in winter in a very inadequately warmed room, it was thought well to arrange to control the temperature of the phosphorus surface at pleasure, and other improvements were made in the experimental arrangement, which is shown in section in fig. 1, and in plan in fig. 2. ($\frac{1}{3}$ actual size.)

The phosphorus is in the form of a sheet or slab, 17 cms. long and 25 mm. broad. It is cast in a groove or recess 1 mm. deep, with under-cut edges to hold it in. This recess is in the outer side of the metal cooling tank. The phosphorus surface, shown dotted in fig. 1, is thus flush with the metal side of the tank, and is approximately at the same temperature as the water in the tank. A sheet of glass is held parallel to the phosphorus surface and at a distance of 1·75 mm. from it. A cardboard packing between the

metal walls and the glass defined their distance, and closed the sides and one end of the channel. The air blast was introduced near the closed end as shown, and passed over the phosphorus surface. Beyond the phosphorus the channel was prolonged at the same depth (1·75 mm.) for about 5·5 cms., and then abruptly deepened to about 8 mm. as shown. The part of the channel beyond the tank was made of wood, but the glass cover was prolonged over the whole length, to afford a view. The phosphorus slab was, of course, in a vertical plane, with its length horizontal.

The temperature in the tank was kept uniform by means of a mechanically

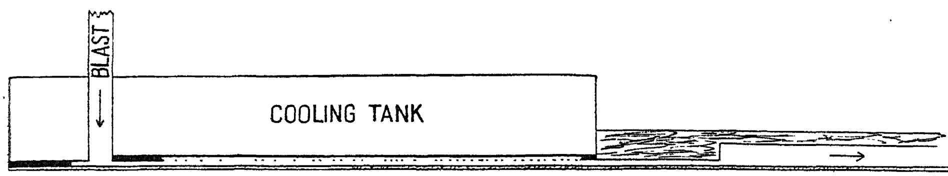


Fig. 1.

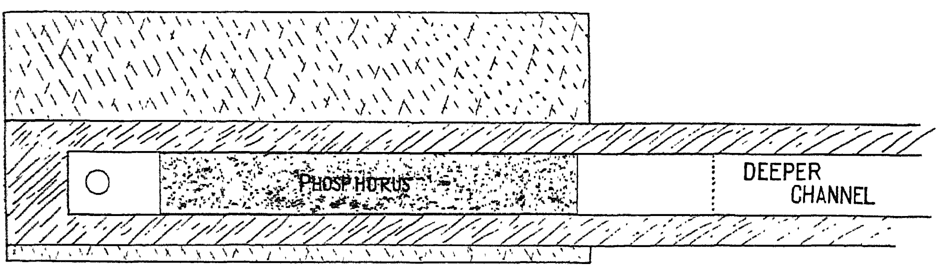


Fig. 2.

driven stirrer, and was maintained at the desired value, usually below the room temperature, by the addition of ice-cold water as required.

With these arrangements, it was soon found that the possibility of blowing off the luminosity was mainly a question of temperature. Using an air blast, it could be done satisfactorily at 10° C., but not at 15° C. Thus the experiment will not succeed in a well-warmed room unless provision is made for cooling the phosphorus surface.

In the original form of experiment, with a cylindrical glass tube, the position of the detached luminosity is somewhat unstable. The luminous cloud, if stationary, remains so because the velocity of propagation of the wave of luminosity through the phosphorus-oxygen mixture is the same as the velocity of the blast, which accordingly neutralises it, and holds the luminous pulse at rest. This point of view is readily verified by slightly checking the velocity of

the blast, when the luminosity travels upstream towards the phosphorus. The exact position of the luminosity is, therefore, only maintained if the blast is absolutely steady, and even so it is only in neutral equilibrium. The sudden deepening of the channel shown in fig. 1 is designed to avoid this difficulty. The blast may be adjusted so as to blow the luminous cloud to the place where the channel has deepened. The luminous cloud will then be unable to retreat upstream towards the phosphorus in the face of the much more rapid gas stream in the narrower channel. On the other hand the stream in the wider channel is not rapid enough to carry it further down. Provided that its velocity of propagation is intermediate between the linear velocity of the gas stream in the narrow channel and in the wide one, its position will be quite stable at the place where the channel widens, independently of strict constancy in the blast. Thus it becomes possible to give the long exposures necessary to photograph the effect.

Plate 26, No. I shows the luminosity of the phosphorus strip when the blast is not acting. No. V shows the luminous cloud blown right off the phosphorus surface. The position of the latter has been indicated by dotted lines marked on the print. The phosphorus itself is absolutely dark. About two hours exposure was given, using a cinematograph lens (F/1·9) and rapid plates.

§3. *Effect of Varying Temperature and Oxygen Concentration.*

When it had been found that the glow could not be blown off at the temperature of 15° C., using an air blast, the oxygen content of the blast was varied and a surprising and instructive result emerged. It was found that with air enriched with oxygen, the luminous cloud could readily be blown away from the phosphorus. When substituting an equally rapid air blast, the luminosity obstinately clung to the phosphorus.

The next step was to determine for comparison the velocity of blast necessary with various oxygen percentages, and at various temperatures, other conditions remaining the same. It would have been possible to adopt, as a standard, the velocity of stream necessary to blow the luminosity right off the phosphorus strip, but experience showed that a more definite measurement could be got of the velocity necessary to blow the glow half way (8·5 cm.) down the phosphorus, leaving the upstream half dark.

It is not difficult to understand why this succeeds best. The current of gas passing over the phosphorus surface becomes increasingly charged with phosphorus vapour. The further the glow is pushed back, the richer in phosphorus vapour will the region immediately upstream of it become. In

this way the tendency of the glow to advance against the stream will be increased, or, in other words, it will become more difficult to push it further downstream. The glow behaves like a spring, which becomes stiffer the further it is pushed back. This leads to a certain stability in the position of the luminous boundary, so long as this *remains on the phosphorus surface.*

The velocity necessary to blow the glow just off was found to be roughly about double that necessary to blow it half way down.

The air or other mixture was contained in a graduated gas holder over water and the discharge determined in c.c. per second. It was converted to cm. per second by a knowledge of the cross section of the channel. The range of velocities encountered was so great that it was necessary to use three gas holders of very different sizes in order to make each measurement in a convenient time, say about one minute. The following are the results :—

Oxygen per cent.		100	73	60	47	20	13	10	1
Linear velocity cm. per sec.	at 15° C.	1·7	9·6	14	44	>990	>990	>990	>990
,,	at 10° C.	E	E	0·88	1·68	99	>990	>990	>990
,,	at 4° C.	E	E	E	1·0	2·4	22	180	>990

The arrangement used did not allow of a more rapid blast than 990 cm. per second. At the higher temperatures or lower oxygen concentrations this was not enough to blow the glow half way off the phosphorus.

At low temperatures and high oxygen concentrations the glow was extinguished altogether by the gentlest blast, and would not come back even when the blast was stopped. Thus no measurement could be made. This result is entered E (Extinction) in the table.

It will be noticed how enormous is the effect of altering the temperature or the oxygen concentration. For instance, at 4° C., we may increase the measured velocity 1,000 times by passing from air to a mixture containing only 1 per cent. of oxygen. Or, using air throughout, we may produce a change of the same order by passing from 4° C. to 15° C.

§4. *Attendant Luminous Effects.*

In making these measurements, modifications were observed in the luminous effects under various conditions, and in order to bring home their striking character to others who may not have the opportunity of seeing them, a series

of photographs was taken (*see* Plate 26). These successive appearances follow the variation of velocity of the blast, measured as above. The same sequence is followed, whether this velocity is diminished by cooling or by increase of oxygen concentration. The brightness is better maintained by the second method.

In taking the photographs the blast was regulated by hand, using a screw valve, and a luminous mark—a small tube of phosphorescent sulphide—to keep the position of the luminosity fixed, in spite of slight variation in the experimental conditions. The condition of blowing the glow exactly half way down the phosphorus strip was not attended to in taking the photographs, the object being to represent the typical luminous phenomena. Two to four hours' exposure was necessary.

When the velocity of blast was 100 cm. per second or more, the glow showed a tendency to cling to particular points on the phosphorus surface, and it was from these points that the luminosity sprang up, spreading out fanwise from them. Plate 26, No. II shows the earlier stage of this, corresponding to, say, 100 cm. per second, giving the left-hand (upstream) edge of the luminosity an angular outline. At higher velocities this effect is much exaggerated, as the glow clings to these singular points, or plague spots as I have sometimes called them, so that it cannot be detached even by a rapid blast. More will be said about this presently. At velocities ranging from 50 to 5 cm. per second, the tendency just mentioned has disappeared, but another curious effect makes its appearance. This is a bright head to the luminosity. Proceeding to a slightly later stage, the head is followed by a dark interval and then a uniform stretch of luminosity as in III. This is the best stage for blowing the luminosity right off, as in V.

At still lower velocities, of the order of 1 cm. per second, a number of further luminous heads develop as in IV. The photograph hardly does justice to the regularity of these heads, some confusion having occurred by unavoidable changes in the conditions during the four hours' exposure.

§5. *Infective Character of the Glow.*

Many of the experiments described, and some others, indicate that the glow of phosphorus is what may be called an infective phenomenon. Like a human epidemic, its first breaking out is due to obscure causes difficult to particularise, but when it has broken out we can trace, and in some measure understand the causes of, its propagation. We can also stop it by measures which are effective, but the secret of whose effectiveness we only understand in part.

In evidence of this, it will be noticed that in the photographs, as we go downstream, the glow sets in abruptly, there being no trace of it upstream of the place of origin. If the gas stream is stopped, the glow is propagated back, with a definite boundary. The most striking case is when the luminosity is detached as in Plate 26, No. V. The luminosity is propagated till it reaches the phosphorus, and then spreads over the latter, quickly or slowly, according to the temperature, and the smallness of oxygen concentration used.

It has already been mentioned that under certain conditions (high temperature or low oxygen content) the glow is found to develop at particular spots on the phosphorus, from which it is difficult to blow it away. A close examination of these spots showed that they were slight depressions in the phosphorus surface, accidentally present. To exaggerate the effect, a hole about 4 mm. diameter was intentionally made in the middle of the phosphorus slab right through its thickness. The temperature was regulated to about 8° C., and an air blast was used. The appearance is seen in Plate 26, No. VI, which shows how the glow starts in the cavity, spreading downstream from this point.

The explanation will be evident from what has already been said. In the cavity there is partial shelter from the blast, and the glow is developed. The passing stream of gas (phosphorus-oxygen mixture) is infected and the glow spreads downstream.

In another experiment, not essentially different, the glow is blown off the phosphorus slab, as in Plate 26, No. V. A second small piece of phosphorus, stuck on a pin, is placed in the wide channel, a considerable distance downstream. When the blast is increased, so as to blow the luminous cloud down to this point, it becomes anchored, as it were, to the small piece of glowing phosphorus. It cannot be detached from it, though the luminosity may be elongated in the downstream direction by a vigorous blast.

§6. *True Nature of the Dark Interval in Blochs' Experiment.*

In the experiments described on p. 326, the velocity of the blast may be taken as measuring the rate at which the glow could propagate itself in a still atmosphere. If the temperature is low, or the blast rich in oxygen, this velocity becomes very small and may be reduced as low as 1 cm. per second. If the process is carried still further, propagation becomes uncertain, and the luminosity is in a constant flicker, even in the absence of a blast, while finally it is unable to maintain itself and the light goes. out: remaining of fair intrinsic brightness till the end.

It is clear from these facts that when the glow is blown right off, as in Plate 26,

No. V (Blochs' experiment), the mixture of phosphorus and oxygen in the dark interval is in the same condition as prevails when phosphorus is *extinguished altogether* by an excess of oxygen, and no absorption of oxygen can be observed volumetrically. There is no preliminary process of chemical change going on. On the contrary, the condition is one of *hang fire*, or, as it is more formally described, *false equilibrium*.

§7. *Mechanism of Inhibition.*

As to the cause of this hang fire, there can be little doubt that it is analogous to the cases examined in the previous paper (*loc. cit.*), the excess of moist oxygen acting like the other inhibiting substances, such as ammonia or the vapour of camphor. It seems surprising at first sight that oxygen, one of the reacting substances, should inhibit the action when present in excess: but when we come to consider the probable mechanism, it will be seen that there is no real additional difficulty. In any case, the inhibiting action does not become conspicuous until oxygen is present in enormous excess of what is needed to burn the phosphorus vapour which is mixed with it.

The view taken of the propagation of the glow is the same as that of the former paper. The first question is, why does one glowing layer of the gas communicate the glow to the next? It was there shown by calculation from the heat of combustion and the known vapour pressure of phosphorus that rise of temperature was not an adequate explanation.

Some alternative view must be sought, and it is found in the suggestion that the products of combustion in one layer *assist the action in the neighbouring layer*. There is nothing improbable in this, for many analogies exist in the class of actions called catalytic. It is well known to those who make use of such actions in industrial chemistry that the catalyst is very easily put out of order, or *poisoned*, and according to the view here taken, the action of inhibiting substances is to do something of this kind.

Assuming the catalyst to be an acid-forming oxide of phosphorus, it is natural that water vapour, and still more ammonia, should act upon it chemically, and spoil its effectiveness. These cases were examined experimentally in the former paper. Substances like camphor must be supposed to unite with or condense upon the particles of phosphoric oxide or other product in some way, just as they do on gaseous ions. Oxygen is known to condense in this way on gaseous ions, and is here assumed also to condense on the particles of phosphoric oxide.

If the catalyst is spoilt, the mechanism by which the glow is propagated

becomes ineffective, and no propagation occurs. Thus, even if chemical combination starts locally, it does not spread, and no appreciable quantity of material is consumed.

If only a fraction of the catalytically active particles are spoilt before they have the opportunity to act, then propagation, though slower, will not be stopped entirely. Thus it becomes clear why the conditions which make the glow slow of propagation should ultimately make it cease. These conditions are lowered temperature and increased oxygen concentration. Both would naturally tend to promote that condensation of gas on the particles of phosphoric oxide which has been postulated.

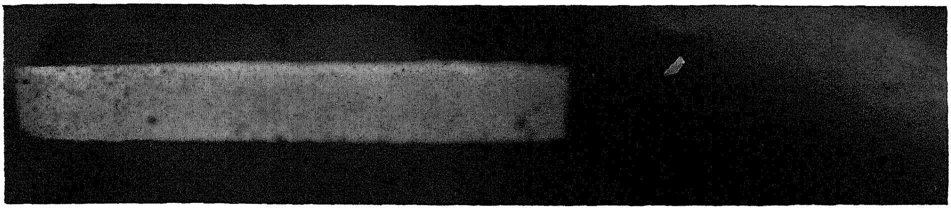
§8. *Discussion of Luminous Heads.*

These are the effects in photographs III and IV, Plate 26, in explanation of which nothing has yet been said.

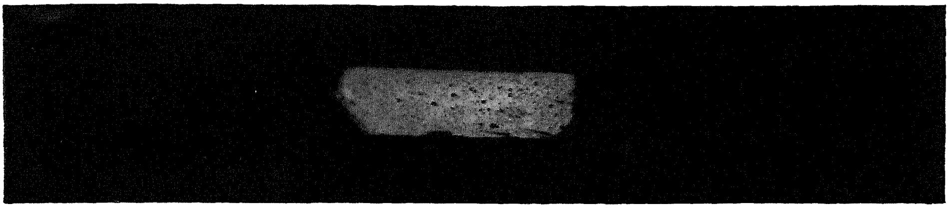
Following the gas current downstream, there will be a certain accumulation of phosphorus vapour, where the glow first appears, for all the vapour which has been collected from the dark part of the surface will now become at once available for chemical action. When this accumulated capital (as it were) has been spent, we are dependent only on the vapour which is collected as the stream proceeds; thus it seems natural that the head should be brighter than any other part of the stream, as in Plate 26, No. III. It is, perhaps, more surprising that this effect should be practically absent in No. II, but it must be remembered that in No. II the blast is much more rapid, and the inhibiting action less strong, so that a smaller stock of phosphorus vapour is collected before the expenditure begins.

In the transition between II and III, where the bright head first becomes distinct, it is followed by uniform luminosity; but in III a dark interval after the head has already made its appearance, separating the head from the remainder of the glow. Though it is not pretended that this would have been foreseen *a priori*, yet it need not cause surprise. The strong glow at the head thoroughly breaks down the inhibiting action by rapid production of catalytic particles, and allows complete and rapid expenditure of the whole stock of phosphorus vapour. After this, the inhibiting action partly recovers its power, owing to the rate of combustion becoming very small, and a further accumulation of phosphorus vapour can occur. This causes a recovery further down. If the inhibiting power is strong enough, this cycle may be repeated, leading to a series of bright heads as in Plate 26, No. IV.

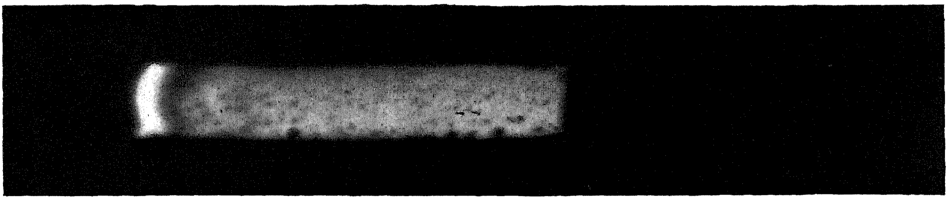
It is recognised that this interpretation is not free from vagueness and



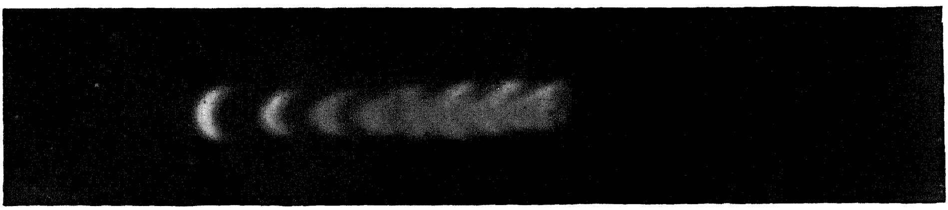
I



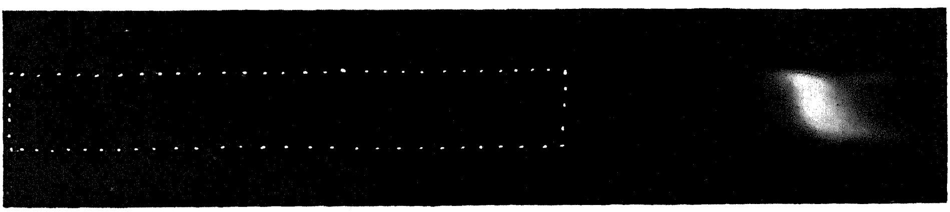
II



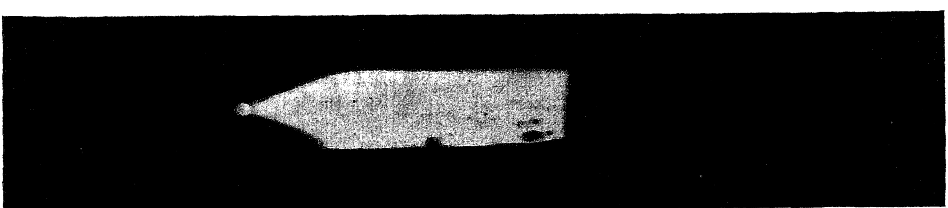
III



IV



V



VI

obscurity. To make it really definite would require a knowledge of the quantitative laws on which a mathematical analysis might be based.*

§9. *Influence of Water Vapour.*

In the experiments described, the air or oxygen mixture was stored over water and thus saturated with water vapour. The surface of the phosphorus was also moist.

It is known† that it is only in moist oxygen that the glow is completely quenched at ordinary temperatures. If the oxygen is dried, *e.g.*, by sulphuric acid, the glow becomes visible, though not very strong.

The apparatus described above (figs. 1 and 2) does not lend itself well to experiments with dried gases. For this purpose a simpler arrangement was used, consisting of a glass U-tube, 6·5 mm. inside diameter, with a strip of phosphorus cast into it, in such a way as to extend along one limb, but only to occupy about half the cross section: thus a stream of oxygen could be passed over the phosphorus.

The phosphorus itself was dried by repeatedly rinsing out the U-tube which contained it with strong sulphuric acid (density 1·835). The phosphorus was left moist with acid, and thus dry as regards water. The oxygen supply was dried with calcium chloride followed by phosphorus pentoxide.

With these arrangements it was found that at 15° C. the phosphorus glowed, and that with the blast of oxygen available only a small fraction of the length could be cleared of glow. At 4° C., the glow still persisted, but could readily be blown right off, and maintained away from the phosphorus, as in Blochs' experiment, Plate 26, No. V.

The tube was then cooled further in a bath of ether to which solid carbon dioxide was added. As the result of several experiments, it was found that the luminosity persisted down to a temperature of about — 20° C. At temperatures a little higher than this it was blown off by a very gentle blast of oxygen and crept back slowly when the blast was stopped.

The final extinction at low temperature (—20° C.) appeared to be definite and abrupt. At these low temperatures the luminosity is faint, and the observations require a perfectly dark room and well rested eyes.

* It will be noticed that Plate 26, No. III is very suggestive of the Crookes' dark space negative glow, Faraday dark space and uniform positive column of a vacuum discharge. IV, too, is very suggestive of the striated positive column. It seems not unlikely that these resemblances depend on a formal analogy between the causes acting in the two cases. The interpretation suggested above has some analogy with explanations which have been given of electrical striations.

† E. J. Russell, 'Trans. Chem. Soc.,' vol. 83, p. 1263 (1903).

The general conclusion is that the phenomena in dry oxygen are similar to those in moist oxygen, but that extinction requires a much lower temperature.

From the point of view adopted above, it would appear that water vapour gives efficient help in the process of condensation which (it is supposed) spoils the catalytic action of the products of combustion and prevents propagation of the action. It would appear that oxygen and water vapour both take part in this inhibiting action, and do more than either can do separately.

We have just seen, however, that excess of oxygen without water can hold up the combustion at low temperatures.

It appears from the results of the former paper (*loc. cit.*) that water alone can hold up the combustion when oxygen is only present in very minute traces. There is room for a further investigation of these points, so as to trace out the phenomena completely when the concentrations of both oxygen and water vapour, and also the temperature, are varied. The effect of extreme drying, as in H. B. Baker's experiment, also requires to be explored.

§10. *Summary.*

It is impossible to deal with all the points in a few lines, but the following are some of the more important.

The velocity of blast necessary to blow away the glow of phosphorus increases enormously with rise of temperature. On the other hand, it is enormously diminished by enriching the air blast with oxygen. In either case the range examined was of the order of 1,000 times.

This velocity of blast measures the rate of propagation upstream of the glow through a mixture of phosphorus vapour and oxygen.

When the velocity is reduced either by cooling or by adding oxygen to less than 1 cm. per second, the condition of extinction is approached. From this point of view the known extinction by an atmosphere of moist oxgyen alone is seen to be the limiting case of slow propagation.

It follows that extinction is due to the failure of the process which causes propagation. This was shown in a former paper to be in all probability a catalytic action of the products of combustion. Excess of oxygen, like other inhibiting substances, "poisons" these products, or makes them unfit to act, perhaps by a process of condensation, similar to that which is found to clog the motion of the ions in gaseous combustion.

On the Complex Anisotropic Molecule in Relation to the Dispersion and Scattering of Light.

By Louis V. King, D.Sc., Macdonald Professor of Physics, McGill University, Montreal.

(Communicated by Prof. A. S. Eve, F.R.S. Received January 1, 1923.)

§ 1. *Introduction.*

It has now been known for several years that the molecules of a gas consisting of positive and negative charges set into forced vibrations by the electric field of an incident light-wave are responsible, not only for the refractive properties of the medium, but also for lateral scattering and extinction as exemplified on a large scale by the blue of the sky and the colour of the setting sun.* In fact, until comparatively recently, observations on the extinction of solar radiation of various wave-lengths by the earth's atmosphere have provided the only data† by means of which the theory of molecular scattering and extinction could be tested, this by satisfactory evaluations of the number of molecules per cubic centimetre of air under standard conditions of temperature and pressure,‡ making use for the purpose of Rayleigh's well-known extinction formula based on the idea of the *symmetrical molecule, i.e.*, one in which the

* Lord Rayleigh, 'Phil. Mag.,' vol. 37, pp. 375–384 (1899).

† 'Annals of the Smithsonian Astrophysical Observatory,' Washington, vols. II (1908) and III (1913).

‡ Schuster, A., 'Nature,' vol. 81, p. 97 (1909). Natanson, L., 'Bull. Int. de l'Acad. des Sciences de Cracovie' (1910). King, L.V., 'Phil. Trans,' vol. 212, A (1912). A comprehensive survey of the entire field is given by Cabannes, J., Thèse, "Sur la diffusion de la lumière par les molécules des gaz transparents," 'Annales de Physique,' vol. 15 (1921). Further references given in this section are, for the most part, supplementary.

dispersion electrons move in the direction of the electric vector in the light-wave.*

As far as observations were then available, theory gave a tolerably good account of measurements of sky-intensity, both as regards quality and polarization.† The difficulty in this case is to take into account the illumination of the atmosphere by itself, a problem capable of reasonably simple solution in terms of integral equations only if the curvature of the earth is disregarded.‡ From the experimental point of view, satisfactory observations are made difficult by the omnipresent and ever-varying dust content of the atmosphere at ordinary levels, to say nothing of the "haziness" and extinction due to the presence of water-vapour.§

For these reasons, observations of atmospheric extinction and polarization were not sufficiently precise to detect effects due to possible molecular anisotropy, until recent laboratory investigations on light scattering in gases revealed a marked departure as regards polarization from theoretical requirements based on symmetrical molecules.

§ 2. *The Anisotropic Molecule.*

That the molecules of a dust-free gas are able to scatter light seems to have been first demonstrated by Cabannes|| in 1913, although the unexpected result of *depolarization* or incomplete polarization was first established by Lord Rayleigh,¶ and substantially verified by the later observations of Cabannes,** in France, and of Gans, in Argentina.††

On rotating the analysing nicol complete extinction is not obtained, and the ratio of the minimum to the maximum is termed the "depolarization," a

* King, L. V., 'Nature,' vol. 93, p. 557 (1914). Fowle, F. E., 'Astrophys. Journ.,' vol. 40, p. 435 (1914). Dember, H., 'Ann. der Physik,' vol. 49, pp. 599–610 (1916). Fowle, 'Smithsonian Miscellaneous Collections,' vol. 69, No. 3, May, 1918).

† In addition to observations by the Smithsonian Astrophysical Observatory ('Annals,' vol. III) we may mention those by Bauer and Moulin, 'Comptes Rendus,' vol. 151, p. 864 (1910), and by Pacini, 'Nuovo Cimento,' vol. 10, pp. 131–167 (1915).

‡ King, L. V., 'Phil. Trans.,' vol. 212, A, p. 380 (1912).

§ In this connection recent observations cited by Raman are of interest ('Nature,' p. 75, Jan. 19, 1922), also "Molecular Diffraction of Light" (Univ. of Calcutta Press, 1922).

|| Cabannes, J., "Sur la diffusion de la lumière par l'air," 'C.R.,' vol. 160, pp. 62–63 (1915).

¶ Strutt, R. J. (Lord Rayleigh), 'Roy. Soc Proc.,' vol. 94, A, p. 453 (1918); vol. 95, A, pp. 155–176 (1919); vol. 95, A, pp. 476–479 (1919).

** Cabannes, J., 'Annales de Physique,' vol. 15 (1921).

†† Gans, R., "Asymmetrie von Gasmolekeln," 'Ann. der Physik,' vol. 65, pp. 97–123 (1921).

quantity characteristic of the gas, determinable with fair accuracy, and indicative of the asymmetry of the molecule.

The simple " asymmetrical " or " anisotropic " molecule seems to have been first discussed in a fundamental paper by Langevin.* In this paper by means also of the statistical theory of fluctuations of " molecular orientations " in electric and magnetic fields he has accounted successfully for the outstanding features of electric and magnetic double refraction.

The simple anisotropic molecule will, in general, have three natural vibration periods, corresponding to the free oscillations along each of the principal axes, while an aggregate of such molecules will possess, in general, three *molecular absorption* bands. But most substances have a much more complicated spectrum, so that the simple anisotropic molecule cannot be expected to account in detail for all the optical properties of transparent media. When, however, it is employed in the classical electromagnetic theory of radiation, in place of the familiar dispersion electron assumed to move in the direction of the electric vector in the light-wave, many optical phenomena are satisfactorily accounted for.

In the following sections there is a systematic discussion of the associated theories of dispersion and scattering based on a general type of complex anisotropic molecule, developed in such a way that the formulae may be applied to scattering in dust-free transparent liquids, recent observations of this phenomena now being available.†

§ 3. *Dispersion Theory in Terms of the Simple Anistropic Molecule.*

The refractive index of a transparent medium is due to the reaction of the positive and negative charges, constituting atoms and molecules, on the propagation of electro-magnetic disturbances.

We will first consider a simple anisotropic molecule, *i.e.*, one containing a

* Langevin, P., " Sur les biréfringences électrique et magnétique," 'Le Radium,' vol. 7, pp. 249–60 (1910).

† Martin, W. H., " The Tyndall Effect in Liquids," 'Roy. Soc. Proc.,' Canada, vol. 7, p. 219 (1913); 'Chem. Abs.,' vol. 8, p. 3739 (1914). " The Scattering of Light by Dust-Free Liquids," 'Journ. Phys. Chem.,' vol. 24, p. 478 (June, 1920); vol. 26, p. 75 (Jan., 1922); " The Relation between Light Absorption and Light Scattering for Liquids," 'Journ. Phys. Chem.,' vol 26, p. 471 (May, 1922). Bibliography, 'Trans. Roy. Soc., Canada,' vol 16, p. 276 (1922).

Kenrick, F. B., 'Journ. Phys. Chem.,' vol 26, p. 72 (Jan., 1922).

Ramanathan, K. R., " The Molecular Scattering of Light in Vapours and in Liquids, etc.," 'Proc. Roy. Soc.,' vol. 102, A, p. 151 (Nov., 1922).

single dispersion electron of mass m, and charge e. This will have three equations of motion of the type—

$$m(\ddot{\xi}+p_1^2\xi) = e(\mathrm{E}_1+\mathrm{P}_1), \tag{1}$$

where E is the electric vector, and P the polarization vector due to all other vibrating electrons in the medium, and ξ, η, ζ are displacements along its three principal axes of vibration (*see* fig. 1).

For periodic displacements due to the electric force in a light wave proportional to e^{ipt}, we have—

$$\xi = (\mathrm{A}/e)(\mathrm{E}_1+\mathrm{P}_1), \quad \eta = (\mathrm{B}/e)(\mathrm{E}_2+\mathrm{P}_2), \quad \zeta = (\mathrm{C}/e)(\mathrm{E}_3+\mathrm{P}_3), \tag{2}$$

where

$$\mathrm{A} = \frac{e^2}{m}\cdot\frac{1}{p_1^2-p^2}, \quad \mathrm{B} = \frac{e^2}{m}\cdot\frac{1}{p_2^2-p^2}, \quad \mathrm{C} = \frac{e^2}{m}\cdot\frac{1}{p_3^2-p^2}. \tag{3}$$

Corresponding to the three natural periods of vibration $2\pi/p_1$, etc., we have the

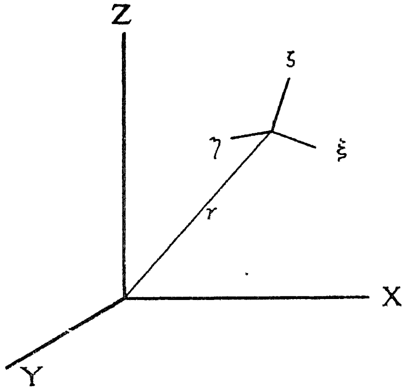


Fig. 1.

wave lengths λ_1, λ_2, λ_3, given by the relations $\lambda_1 = 2\pi c/p_1$, ..., where c is the velocity of light in vacuo.

Referred to axes (X, Y, Z) fixed in the medium, we denote by—

$$\mathrm{Z}(x, t) = |\mathrm{Z}|\cos p(t-x/c) = |\mathrm{Z}|\cos(pt-2\pi x/\lambda) \tag{4}$$

the electric force parallel to the axis of Z due to a plane-polarized light-wave acting on the molecule at P, whose co-ordinates are (x, y, z). This electric force displaces all the electrons of the molecules giving rise to a polarized field $\mathrm{Z}_p(x, t)$ which in isotropic media is assumed parallel to $\mathrm{Z}(x, t)$, and depends only on the molecules in the immediate neighbourhood of P so that $\mathrm{Z}_p(x, t)$ and $\mathrm{Z}(x, t)$ do not differ appreciably in phase.

In these circumstances, resolving along (ξ, η, ζ) whose direction cosines relative to X, Y, Z are—

$$(l_1, m_1, n_1), \qquad (l_2, m_2, n_2), \qquad (l_3, m_3, n_3),$$

we have

$$E_1 = n_1 Z, \qquad E_2 = n_2 Z, \qquad E_3 = n_3 Z,$$
$$P_1 = n_1 Z_p, \qquad P_2 = n_2 Z_p, \qquad P_3 = n_3 Z_p,$$

so that the components of the displacement are—

$$\xi = (A/e)\, n_1 (Z + Z_p), \quad \eta = (B/e)\, n_2 (Z + Z_p), \quad \zeta = (C/e)\, n_3 (Z + Z_p). \quad (5)$$

The potential at O, the origin, due to the displacement of the charge e at P will be denoted by $\Omega(x, t+r/c)$, so that the polarization field at O due to all the molecules of the medium is given by—

$$Z_p(o, t+r/c) = \Sigma\, (\partial/\partial z)\, \Omega\, (x, t+r/c). \quad (6)$$

The calculation of the polarization field as represented by the summation (6) constitutes one of the most difficult problems of dispersion-theory. Following the classical treatment of Lorentz,* we have for molecules near O in a sphere of radius a, small compared with a wave length—

$$\Sigma\, (\partial/\partial z)\, \Omega\, (x, t) = s\, [Z(o, t) + Z_p(o, t)] \quad (7)$$

where s is zero or small and dependent on wave length and temperature.

The remaining part of the summation gives rise to a volume integral, which may be transformed by Green's theorem into (1) an integral to be taken over the surface of the sphere of radius a, (2) a similar integral over the surface of the dispersing medium, and (3) an integral taken over the volume between these two surfaces. The two latter integrals vanish. The integral over the surface of the sphere of radius a is equal to—

$$\tfrac{4}{3}\pi n_0 \bar{k}\, [Z(o, t) + Z_p(o, t)]$$

where n_0 = average number of molecules or dispersion electrons per cm.^{3} and $\bar{k} = A\bar{n_1^2} + B\bar{n_2^2} + C\bar{n_3^3}$, bars denoting average values. Hence, the total polarization field as given by (6) is—

$$Z_p = (\tfrac{4}{3}\pi n_0 \bar{k} + s)\, [Z + Z_p] \quad (8)$$

where Z, Z_p now denote Z (o, t) and Z_p (o, t) respectively.

Adding the convection current due to the dispersion electrons to the Maxwell displacement current, the total current density along the Z-axis is—

$$w = \frac{1}{4\pi}\frac{dZ}{dt} + n_0 \bar{k}\frac{d}{dt}\, [Z + Z_p]. \quad (9)$$

* Lorentz, H. A., "The Theory of Electrons" ('Teubner's,' 1909), pp. 137–152; also pp. 302–306. The subject of dispersion is discussed at great length by Lundblad, R., "Untersuchungen über die Optik der dispergierenden Medien von molekulartheoretischen Standpunkte" (Thesis, 'Publications of the University of Upsala,' 1920).

From (8) and (9) we obtain—

$$w = \frac{\mu^2}{4\pi}\frac{dZ}{dt} \tag{10}$$

where
$$\frac{3(\mu^2-1)}{\mu^2+2} = \frac{4\pi n_0 \bar{k}}{1-s} \tag{11}$$

and
$$\frac{Z+Z_p}{Z} = \frac{\mu^2+2}{3}\cdot\frac{1}{1-s} = \frac{\mu^2-1}{4\pi n_0 \bar{k}}. \tag{12}$$

Equation (11) leads to the well-known dispersion formula of the Lorentz type, and Havelock* has shown that (with $s = 0$, and $\lambda_2 = \lambda_3$, *i.e.* $p_2 = p_3$) Kirn's† observations on dispersion in Hydrogen are thereby accurately interpreted, while the calculated value of the depolarization agrees closely with Lord Rayleigh's‡ experimental determination.

§ 4. *Scattering of Light by a Simple Anisotropic Molecule.*

We proceed, now, to investigate the light scattered by an anisotropic molecule situated at the origin O (fig. 2). As before, we suppose that the incident light

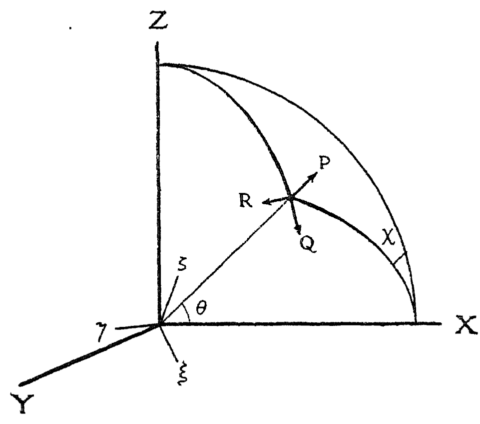


Fig. 2.

is propagated along the X-axis and is plane-polarized, the electric vector being parallel to the Z-axis. It will be remembered that in a plane-polarized electromagnetic wave, the electric force (light vector) is perpendicular to the plane of polarization.

* Havelock, T. H., 'Roy. Soc. Proc.,' vol. 101, A, pp. 154–164 (1922). A formula of this type is implied in a paper by Langevin on electric and magnetic double refraction ('Le Radium,' vol 7, p. 255 (1910), equation (36)), although no comparison is made with experiment.

† Kirn, M., 'Ann. de Phys.,' vol. 64, pp. 556–576 (1921).

‡ Lord Rayleigh, 'Roy. Soc. Proc.,' vol. 97, A, p. 449 (1920).

The principal axes (ξ, η, ζ) of the molecule are defined as before in section 3. In examining the light scattered to a distant point P, we take POX as the plane of reference. The scattered wave at P is completely specified by the electric vector P along OP, Q perpendicular to the plane POX, and R perpendicular to both P and Q. The direction cosines of the mutually perpendicular vectors P, Q, R are given by the table—

	P	Q	R
X	$\cos\theta$	0	$-\sin\theta$
Y	$\sin\theta\sin\chi$	$\cos\chi$	$\cos\theta\sin\chi$
Z	$\sin\theta\cos\chi$	$-\sin\chi$	$\cos\theta\cos\chi$

(13)

θ and χ being the angles indicated in fig. 2.

If $(\alpha_p, \alpha_q, \alpha_r)$ be the components of acceleration parallel to (P, Q, R) of a moving charge at O, the electrical intensities in the resulting spherical wave are given by*

$$\mathrm{P}=0, \quad \mathrm{Q}=-\frac{e}{c^2 r}\alpha_q, \quad \mathrm{R}=-\frac{e}{c^2 r}\alpha_r, \tag{14}$$

provided velocities and accelerations remain within the limits of *quasi*-stationary motion.

From equation (5) it is seen that the components of acceleration of the charge e along the axes (ξ, η, ζ) are—

$$\ddot{\xi}=-p^2(\mathrm{A}/e)\,n_1(\mathrm{Z}+\mathrm{Z}_p), \quad \ddot{\eta}=-p^2(\mathrm{B}/e)\,n_2(\mathrm{Z}+\mathrm{Z}_p),$$
$$\ddot{\zeta}=-p^2(\mathrm{C}/e)\,n_3(\mathrm{Z}+\mathrm{Z}_p). \tag{15}$$

Since

$$\left.\begin{aligned}\alpha_q &= \ddot{\xi}\cos\widehat{\xi\mathrm{Q}}+\ddot{\eta}\cos\widehat{\eta\mathrm{Q}}+\ddot{\zeta}\cos\widehat{\zeta\mathrm{Q}}\\ \alpha_r &= \ddot{\xi}\cos\widehat{\xi\mathrm{R}}+\ddot{\eta}\cos\widehat{\eta\mathrm{R}}+\ddot{\zeta}\cos\widehat{\zeta\mathrm{R}}\end{aligned}\right\} \tag{16}$$

and

$$\cos\widehat{\xi\mathrm{Q}}=\cos\widehat{\xi\mathrm{X}}\,.\,\cos\widehat{\mathrm{XQ}}+\cos\widehat{\xi\mathrm{Y}}\,.\,\cos\widehat{\mathrm{YQ}}+\cos\widehat{\xi\mathrm{Z}}\,.\,\cos\widehat{\mathrm{ZQ}},$$

with similar equations for the remaining cosines in (16), we find from (13)—

$$\left.\begin{aligned}\mathrm{P}=0, \quad \mathrm{Q}&=\frac{p^2}{c^2 r}(\mathrm{Z}+\mathrm{Z}_p)(j\cos\chi-k\sin\chi)\\ \mathrm{R}&=\frac{p^2}{c^2 r}(\mathrm{Z}+\mathrm{Z}_p)(-h\sin\theta+j\cos\theta\sin\chi+k\cos\theta\cos\chi)\end{aligned}\right\} \tag{17}$$

where

$$\left.\begin{aligned}h&=\mathrm{A}n_1l_1+\mathrm{B}n_2l_2+\mathrm{C}n_3l_3\\ j&=\mathrm{A}n_1m_1+\mathrm{B}n_2m_2+\mathrm{C}n_3m_3\\ k&=\mathrm{A}n_1^2+\mathrm{B}n_2^2+\mathrm{C}n_3^2\end{aligned}\right\} \tag{18}$$

* Lorentz, H. A., 'The Theory of Electrons' (Teubner's, 1909), art. 39, p. 51.

Squaring and adding, we have the relation,

$$h^2 + j^2 + k^2 = A^2 n_1^2 + B^2 n_2^2 + C^2 n_3^2. \tag{19}$$

It is easily seen that on averaging for a law of distribution of molecular orientations unaltered by changes in sign of the direction cosines (*e.g.*, depending on their squares), we have—

$$\overline{jk} = 0, \quad \overline{kh} = 0, \quad \overline{hj} = 0. \tag{20}$$

Furthermore, if the law of distribution depends only on the angles which the principal axes of the molecule make with the Z-axis, *i.e.*, on (n_1, n_2, n_3) (as in problems of electric and magnetic double refraction), the average values $\overline{h^2}$ and $\overline{j^2}$ are unaltered by interchanging the axes X and Y, or (l_1, l_2, l_3) and (m_1, m_2, m_3) so that $\overline{h^2} = \overline{j^2}$. In these circumstances we have from (19)

$$\left.\begin{aligned} 2\overline{h^2} + \overline{k^2} &= A^2\overline{n_1^2} + B^2\overline{n_2^2} + C^2\overline{n_3^2} \\ \text{where, from (18),} \qquad \overline{k^2} &= A^2\overline{n_1^4} + B^2\overline{n_2^4} + C^2\overline{n_3^4} + 2BC\overline{n_2^2 n_3^2} \\ &\quad + 2CA\overline{n_3^2 n_1^2} + 2AB\overline{n_1^2 n_2^2} \end{aligned}\right\}. \tag{21}$$

Since the axes (ξ, η, ζ) may, in an *isotropic distribution* of molecular orientations, be mutually interchanged without affecting the final result of averaging, we have, since

$$\begin{aligned} \overline{n_1^2} + \overline{n_2^2} + \overline{n_3^2} &= 1, \\ \overline{n_1^2} = \overline{n_2^2} = \overline{n_3^2} &= \tfrac{1}{3}. \end{aligned} \tag{22}$$

Furthermore,

$$\overline{n_1^4} = \overline{n_2^4} = \overline{n_3^4} = \tfrac{1}{2}\int_0^\pi \cos^4\theta \sin\theta \, d\theta = \tfrac{1}{5}, \tag{23}$$

and, since

$$\begin{aligned} \overline{n_1^4} + \overline{n_2^4} + \overline{n_3^4} + 2\overline{n_2^2 n_3^2} + 2\overline{n_3^2 n_1^2} + 2\overline{n_1^2 n_2^2} &= 1 \\ \overline{n_1^2 n_2^2} = \overline{n_2^2 n_3^2} = \overline{n_3^2 n_1^2} &= \tfrac{1}{15}. \end{aligned} \tag{24}$$

Thus, for *equally probable molecular orientations*,* it follows from (12) that

$$\left.\begin{aligned} &2\overline{h^2} + \overline{k^2} = \tfrac{1}{3}\Sigma A^2, \quad \overline{k^2} = \tfrac{1}{15}(3\Sigma A^2 + 2\Sigma BC) \\ \text{when} \qquad &\Sigma A^2 = A^2 + B^2 + C^2 \quad \text{and} \quad \Sigma BC = BC + CA + AB. \end{aligned}\right\} \tag{25}$$

* The results of averaging for equally probable molecular orientations obtained in this section are in agreement with those of the late Lord Rayleigh, obtained by direct integrations in terms of the Eulerian angles (Lord Rayleigh, 'Phil. Mag.,' vol 25, pp. 373–381 (1918). 'Scientific Papers,' vol VI, pp. 540–548).

It is convenient to introduce the ratio ρ defined by the relation

$$\rho = \frac{2\overline{h^2}}{\overline{h^2}+\overline{k^2}} = \frac{2(\Sigma A^2 - \Sigma BC)}{4\Sigma A^2 + \Sigma BC}. \tag{26}$$

From the last equation of (18) and (22) we have

$$\bar{k} = \tfrac{1}{3}(A+B+C). \tag{27}$$

Eliminating ΣA^2 and ΣBC between (25), (26) and (27) we obtain

$$\overline{h^2} = \overline{j^2} = 3(\bar{k})^2 \cdot \frac{\rho}{6-7\rho}, \quad \overline{k^2} = 3(\bar{k})^2 \cdot \frac{2-\rho}{6-7\rho} \tag{28}$$

and

$$3\overline{k^2} - 4\overline{h^2} = 3(\bar{k})^2. \tag{29}$$

§ 5. *Dispersion Theory in terms of the Complex Anisotropic Molecule.*

(i) *Monomolecular Media.*—It is hardly to be supposed that the simple anisotropic molecule dealt with in the preceding sections can represent the actual state of affairs in any physical medium. We proceed, therefore, to consider a more general type of molecule made up of any number of positive and negative charges (referred to as dispersion charges) in static equilibrium under the mutual action of intermolecular forces.* Without specifying the exact nature of these forces about which we are still in ignorance, we will suppose that the system is stable for small displacements, and that each charge is capable of vibration about its equilibrium position. For each dispersion charge three axes may be found with respect to which the equations of motion are given by equation (1). These *principal directions* will not, however, be parallel for all the dispersion charges affected by the incident light-wave.

We denote, by the following table, the direction cosines of the principal directions of the ith dispersion charge with respect to the axes (X, Y, Z) fixed in the medium.

$$\begin{array}{c|ccc} & \xi_i & \eta_i & \zeta_i \\ \hline X & {}^il_1 & {}^il_2 & {}^il_3 \\ Y & {}^im_1 & {}^im_2 & {}^im_3 \\ Z & {}^in_1 & {}^in_2 & {}^in_3 \end{array} . \tag{30}$$

* The writer has thought it desirable in the sequel to use the term *dispersion charge* in preference to *dispersion electron,* to denote the positive and negative parts of atomic systems which, by their vibrations in the periodic electric field of a light-wave, give rise to the phenomenon of dispersion.

Since the results of § 3 apply to the ith dispersion charge in each molecule of an aggregate, its contribution to the polarization field at O is, by (8)—

$$ {}^{i}Z_p = (\tfrac{4}{3}\pi n_0 \bar{k}_i + s_i)\,[Z+Z_p], \tag{31} $$

where

$$ \bar{k}_i = A_i \overline{{}^{i}n_1{}^2} + B_i \overline{{}^{i}n_2{}^2} + C_i \overline{{}^{i}n_3{}^2}, \tag{32} $$

and s_i is defined by (7) with respect to the ith dispersion electron.

The total polarization field due to the i dispersion charges in each molecule of which there are n_0 per unit volume is given by—

$$ Z_p = \sum_i Z_p = (Z+Z_p) \sum_i (\tfrac{4}{3}\pi n_0 \bar{k}_i + s_i). \tag{33} $$

Similarly, the total current density along the Z-axis is, as in (17),

$$ w = \frac{1}{4\pi}\frac{dz}{dt} + n_0 \{\sum_i \bar{k}_i\} \frac{d}{dt}[Z+Z_p]. \tag{34} $$

Writing

$$ \overline{K} = \sum_i \bar{k}_i \quad \text{and} \quad S = \sum_i s_i, \tag{35} $$

we finally obtain the formulae—

$$ \frac{3(\mu^2-1)}{\mu^2+2} = \frac{4\pi n_0 \sum_i \bar{k}_i}{1-\sum_i s_i} = \frac{4\pi n_0 \overline{K}}{1-S}, \tag{36} $$

and

$$ \frac{Z+Z_p}{Z} = \frac{\mu^2+2}{3}\cdot\frac{1}{1-\sum_i s_i} = \frac{\mu^2-1}{4\pi n_0 \sum_i \bar{k}_i} = \frac{\mu^2-1}{4\pi n_0 \overline{K}}, \tag{37} $$

corresponding to (11) and (12) for the simple anisotropic molecule.

For an isotropic distribution of molecular orientations, we have*

$$ \overline{{}^{i}n_1{}^2} = \overline{{}^{i}n_2{}^2} = \overline{{}^{i}n_3{}^2} = \tfrac{1}{3} $$

for all values of i, so that (36) leads to a general dispersion formula of the Lorentz type, applicable to a medium made up of complex anisotropic molecules having $3i$ absorption bands—

$$ \frac{3(\mu^2-1)}{\mu^2+2} = \frac{e^2 n_0}{3\pi c^2 m(1-\sum_i s_i)} \sum_i \left[\frac{1}{{}^{i}\lambda_1{}^{-2}-\lambda^{-2}} + \frac{1}{{}^{i}\lambda_2{}^{-2}-\lambda^{-2}} + \frac{1}{{}^{i}\lambda_3{}^{-2}-\lambda^{-2}}\right]. \tag{38} $$

If the values of e_i^2/m for the dispersion charges are not all equal, it is readily seen that we have only to write the terms e_i^2/m_i under the summation sign in (38).

(ii) *Mixtures and Compounds.*—The summations in (33) and (34) may be extended to include the dispersion charges belonging to different molecules of

* *See* equation (52) *infra*.

a mixture, or different atoms of a compound. We obtain for (36) and (37) the equations—

$$\frac{3(\mu^2-1)}{(\mu^2+2)} = \frac{4\pi\sum_r n_r \overline{K}_r}{1-\sum_r S_r} \text{ and } \frac{Z+Z_p}{Z} = \frac{\mu^2+2}{3} \cdot \frac{1}{1-\sum_r S_r} = \frac{\mu^2-1}{4\pi\sum_r n_r \overline{K}_r}, \quad (39)$$

the summations $\sum_r$ being extended to include the number of different kinds of molecules concerned, there being n_r per unit volume of each. We denote by μ_r the refractive index of the constituent r alone, when the molecular density is N_r, the molecular weight m_r and the mass density D_r. Then, provided that mixture or chemical combination has no appreciable effect on the (A, B, C)'s of equation (3) owing to molecular (or atomic) interaction, we have for that constituent—

$$\frac{3(\mu_r^2-1)}{\mu_r^2+2} = \frac{4\pi N_r \overline{K}_r}{1-S_r}. \quad (40)$$

The molecular refractivity of the constituent r is defined by the relation—

$$M_r = \frac{m_r}{D_r} \cdot \frac{\mu_r^2-1}{\mu_r^2+2}. \quad (41)$$

Since $D_r = m_r N_r$, we see from (40) that

$$\tfrac{4}{3}\pi \overline{K}_r = (1-S_r) M_r. \quad (42)$$

If w_r is the weight of the constituent r per unit volume of the mixture or compound of density D, we have—

$$w_r = m_r n_r, \quad D = \sum_r w_r, \quad n_r/N_r = w_r/D_r. \quad (43)$$

Furthermore, if τ_r denotes the proportion of each constituent by weight, we have

$$\tau_r = w_r / (\sum_r w_r) = w_r/D. \quad (44)$$

From (39) we have on making use of (41), (43), (44)—

$$\frac{1}{D}\frac{\mu^2-1}{\mu^2+2} = \frac{\sum_r \left[\frac{\tau_r(1-S_r)}{D_r}\frac{\mu_r^2-1}{\mu_r^2+2}\right]}{1-\sum_r S_r}. \quad (45)$$

For a large number of substances it is found experimentally that the additive law of Lorentz

$$\frac{1}{D}\frac{\mu^2-1}{\mu^2+2} = \sum_r \frac{\tau_r}{D_r}\frac{\mu_r^2-1}{\mu_r^2+2} \quad (46)$$

holds to a high degree of accuracy.*

* Chéneveau, 'Les propriétés optiques des solutions' (Gauthier-Villars, 1913).

On comparing (45) and (46) it would appear that for each of the constituents the term S_r is negligibly small if not actually zero, a result which is difficult to justify theoretically and which must have some physical significance connected with the geometrical configuration of dispersion electrons in molecules of media in the liquid state.

The formula (39), (45) and (46) also apply when the different molecules (or atoms) form a compound, provided that the inter-atomic forces representing chemical combination have a negligible effect on the (A, B, C)'s of equation (3). If there are c_r atoms of type r for which the *atomic refractivity* is specified by M_r of (42), we see that (39) leads to the result for the molecular refractivity of the compound M,

$$\frac{m}{D}\frac{\mu^2-1}{\mu^2+2} = M = \frac{\sum_r c_r (1-S_r) M_r}{1-\sum_r S_r} \tag{47}$$

where the molecular weight of the compound m is given by—

$$m = \sum_r c_r m_r, \qquad \text{and} \qquad \tau_r = c_r m_r/m.$$

It is found experimentally that the terms S_r are negligible for a large number of substances, when (47) takes the simple form—

$$M = \sum_r c_r M_r.$$

The atomic refractivities M_r cannot be measured directly, but are indirectly calculated from the known refractive indices of compounds. The subject is fully discussed in an interesting paper by Silberstein.*

§ 6. *Scattering of Light by a Complex Anisotropic Molecule.*

If we have several dispersion charges in a complex molecule, each will contribute to the components (P, Q, R) of the scattered radiation amounts given by equations (17) and (18). Hence taking a summation for all the dispersion charges the components of electric force in the radiation scattered by a complex molecule is given by—

$$\left.\begin{aligned} P = 0,\ Q &= \frac{p^2}{c^2 r}(Z+Z_p)(J\cos\chi - K\sin\chi) \\ R &= \frac{p^2}{c^2 r}(Z+Z_p)(-H\sin\theta + J\cos\theta\sin\chi + K\cos\theta\cos\chi) \end{aligned}\right\} \tag{48}$$

* Silberstein, L., "Molecular Refractivity and Atomic Interaction," 'Phil. Mag.,' vol. 33, pp. 92–128 (Jan., 1917).

where

$$\left.\begin{aligned} H &= \sum_i h_i = \sum_i (A_i{}^i n_1{}^i l_1 + B_i{}^i n_2{}^i l_2 + C_i{}^i n_3{}^i l_3) \\ J &= \sum_i j_i = \sum_i (A_i{}^i n_1{}^i m_1 + B_i{}^i n_2{}^i m_2 + C_i{}^i n_3{}^i m_3) \\ K &= \sum_i k_i = \sum_i (A_i{}^i n_1{}^2 + B_i{}^i n_2{}^2 + C_i{}^i n_3{}^2) \end{aligned}\right\}. \tag{49}$$

The principal directions of each dispersion charge will not, in general, be parallel. We refer them to *molecular axes* (ξ, η, ζ) fixed in the molecule, whose direction cosines with respect to X, Y, Z) and (ξ_i, η_i, ζ_i) respectively are given the tables—

$$\begin{array}{c|ccc} & \xi & \eta & \zeta \\ \hline Y & l_1 & l_2 & l_3 \\ X & m_1 & m_2 & m_3 \\ Z & n_1 & n_2 & n_3 \end{array} \qquad \begin{array}{c|ccc} & \xi & \eta & \zeta \\ \hline \xi_1 & {}^i a_1 & {}^i b_1 & {}^i c_1 \\ \eta_1 & {}^i a_2 & {}^i b_2 & {}^i c_2 \\ \zeta_1 & {}^i a_3 & {}^i b_3 & {}^i c_3 \end{array}. \tag{50}$$

The direction cosines in (49) are connected with these of the axes (ξ, η, ζ) by the linear relations—

$$\left.\begin{aligned} {}^i l_r &= {}^i a_r l_1 + {}^i b_r l_2 + {}^i c_r l_3 \\ {}^i m_r &= {}^i a_r m_1 + {}^i b_r m_2 + {}^i c_r m_3 \\ {}^i n_r &= {}^i a_r n_1 + {}^i b_r n_2 + {}^i c_r n_3 \end{aligned}\right\} r = 1, 2, 3. \tag{51}$$

In order to obtain an expression for the intensity of radiation scattered in a particular direction, we have to compute $H^2 + J^2 + K^2$ from (49) and average for all possible orientations of the molecular axes (ξ, η, ζ).

We find as a typical term

$$\begin{aligned} H^2 = \sum_i [&A_i^2{}^i n_1^2{}^i l_1^2 + B_i^2{}^i n_2^2{}^i l_2^2 + C_i^2{}^i n_3^2{}^i l_3^2 + 2B_iC_i{}^i n_2{}^i n_3{}^i l_2{}^i l_3 + \ldots + \ldots] \\ &+ 2\sum_i\sum_s [A_i{}^i n_1{}^i l_1 + B_i{}^i n_2{}^i l_2 + C_i{}^i n_3{}^i l_3][A_s{}^s n_1{}^s l_1 + B_s{}^s n_2{}^s l_2 + C_s{}^s n_3{}^s l_3], \end{aligned}$$

where in the double summation $i = 1, 2, 3, \ldots m$ and $s = 1, 2, 3 \ldots m$, the values $r = s$ being excluded.

Expressions for J^2 and K^2 may be written down from the above by replacing the l's successively by m's and n's.

From (30) we have

$$\cos \widehat{\xi_i \eta_s} = {}^i l_1{}^s l_2 + {}^i m_1{}^s m_2 + {}^i n_1{}^s n_2 \quad (i \neq s)$$

with similar expressions obtained by rotating $(\xi_i \eta_i \zeta_i)$ with the suffixes (1, 2, 3) of the direction cosines $({}^i l_r, {}^i m_r, {}^i n_r)$, and independently (ξ_s, η_s, ζ_s) with the suffixes (1, 2, 3) of $({}^s l_r, {}^s m_r, {}^s n_r)$, where $r = 1, 2, 3$.

Making use of the well-known relations between direction cosines in (30) we find

$$\mathrm{H}^2+\mathrm{J}^2+\mathrm{K}^2 = \sum_i [\mathrm{A}_i^2\,{}^in_1^2 + \mathrm{B}_i^2\,{}^in_2^2 + \mathrm{C}_i^2\,{}^in_3^2]$$

$$+2\sum_i\sum_s [\mathrm{A}_i\mathrm{A}_s\,{}^in_1\,{}^sn_1 \cos \widehat{\xi_i\xi_s} + \mathrm{B}_i\mathrm{B}_s\,{}^in_2\,{}^sn_2 \cos \widehat{\eta_i\eta_s} + \mathrm{C}_i\mathrm{C}_s\,{}^in_3\,{}^sn_3 \cos \widehat{\zeta_i\zeta_s}$$

$$+ \mathrm{B}_i\mathrm{C}_s\,{}^in_2\,{}^sn_3 \cos \widehat{\eta_i\zeta_s} + \text{two similar terms}$$

$$+ \mathrm{B}_s\mathrm{C}_i\,{}^sn_2\,{}^in_3 \cos \widehat{\eta_s\zeta_i} + \text{two similar terms}].$$

On proceeding to average for an isotropic distribution of molecular axes, we easily see from (51), making use of (22), that

$$\overline{{}^in_1^2} = \overline{{}^in_2^2} = \overline{{}^in_3^2} = \tfrac{1}{3}$$

and

$$\overline{{}^in_2\,{}^sn_3} = \tfrac{1}{3}({}^ia_2\,{}^sa_3 + {}^ib_2\,{}^sb_3 + {}^ic_2\,{}^sc_3) = \tfrac{1}{3}\cos \widehat{\eta_i\zeta_s}, \text{ \&c.} \tag{52}$$

Making use of the notation

$$\sum_i\sum_s (\mathrm{A}_i\mathrm{B}_i\mathrm{C}_i)(\mathrm{A}_s\mathrm{B}_s\mathrm{C}_s)\cos^2(\xi_i\eta_i\zeta_i)(\xi_s\eta_s\zeta_s)$$

$$= \sum_i\sum_s [\mathrm{A}_i\mathrm{A}_s \cos^2 \widehat{\xi_i\xi_s} + \mathrm{B}_i\mathrm{B}_s \cos^2 \widehat{\eta_i\eta_s} + \mathrm{C}_i\mathrm{C}_s \cos^2 \widehat{\zeta_i\zeta_s}$$

$$+ \mathrm{B}_i\mathrm{C}_s \cos^2 \widehat{\eta_i\zeta_s} + \mathrm{C}_i\mathrm{A}_s \cos^2 \widehat{\zeta_i\xi_s} + \mathrm{A}_i\mathrm{B}_s \cos^2 \widehat{\xi_i\eta_s}$$

$$+ \mathrm{B}_s\mathrm{C}_i \cos^2 \widehat{\eta_s\xi_i} + \mathrm{C}_s\mathrm{A}_i \cos^2 \widehat{\zeta_s\xi_i} + \mathrm{A}_s\mathrm{B}_i \cos^2 \widehat{\xi_s\eta_i}], \tag{53}$$

we find after some reductions

$$\overline{\mathrm{H}^2}+\overline{\mathrm{J}^2}+\overline{\mathrm{K}^2} = \tfrac{1}{3}\sum_i [\mathrm{A}_i^2+\mathrm{B}_i^2+\mathrm{C}_i^2]$$

$$+ \tfrac{2}{3}\sum_i\sum_s (\mathrm{A}_i\mathrm{B}_i\mathrm{C}_i)(\mathrm{A}_s\mathrm{B}_s\mathrm{C}_s)\cos^2(\xi_i\eta_i\zeta_i)(\xi_s\eta_s\zeta_s). \tag{54}$$

From (49) and (51) we notice that the averaged product terms vanish, *i.e.*

$$\overline{\mathrm{HJ}} = 0, \quad \overline{\mathrm{JK}} = 0, \quad \overline{\mathrm{KH}} = 0. \tag{55}$$

Furthermore, since H is the same function of (l_1, l_2, l_3) as J is of (m_1, m_2, m_3), it follows as in § 4 that—

$$\overline{\mathrm{H}^2} = \overline{\mathrm{J}^2}. \tag{56}$$

From equations (32), (35) and (52) we see that

$$\overline{\mathrm{K}} = \tfrac{1}{3}\sum_i (\mathrm{A}_i + \mathrm{B}_i \quad \mathrm{C}\ ). \tag{57}$$

Squaring the expression for K in (49), we find

$$\mathrm{K}^2 = \sum_i (\mathrm{A}_i^2\,{}^in_1^4 + \mathrm{B}_i^2\,{}^in_2^4 + \mathrm{C}_i^2\,{}^in_3^4)$$

$$+ 2\sum_i [\mathrm{B}_i\mathrm{C}_i\,{}^in_2^2\,{}^in_3^2 + \mathrm{C}_i\mathrm{A}_i\,{}^in_3^2\,{}^in_1^2 + \mathrm{A}_i\mathrm{B}_i\,{}^in_1^2\,{}^in_2^2]$$

$$+ 2\sum_i\sum_s [\mathrm{A}_i\,{}^in_1^2 + \mathrm{B}_i\,{}^in_2^2 + \mathrm{C}_s\,{}^in_3^2][\mathrm{A}_s\,{}^sn_1^2 + \mathrm{B}_s\,{}^sn_2^2 + \mathrm{C}_s\,{}^sn_3^2], \tag{58}$$

where $i = 1, 2, 3 \cdots m$, $s = 1, 2, 3 \cdots m$, and $i \neq s$ in the double summation.

From (60) we have as a typical squared product term

$$ {}^in_1^2\,{}^sn_2^2 = [({}^ia_1n_1^2 + {}^ib_1n_2^2 + {}^ic_1n_3^2) + 2({}^ib_1{}^ic_1n_2n_3 + {}^ic_1{}^ia_1n_3n_1 + {}^ia_1{}^ib_1n_1n_2)] $$
$$ \times [({}^sa_2n_1^2 + {}^sb_2n_2^2 + {}^sc_2n_3^2) + 2({}^sb_2{}^sc_2n_2n_3 + {}^sc_2{}^sa_2n_3n_1 + {}^sa_2{}^sb_2n_1n_2)]. $$

Remembering, from (23) and (24), that

$$ \overline{n_1^4} = \overline{n_2^4} = \overline{n_3^4} = \tfrac{1}{5} \quad \text{and} \quad \overline{n_2^2n_3^2} = \overline{n_3^2n_1^2} = \overline{n_1^2n_3^2} = \tfrac{1}{15}, \qquad (59) $$

we find on averaging the above expression for an isotropic distribution of molecular axes

$$ \overline{{}^in_1^2\,{}^sn_2^2} = ({}^ia_1^2\,{}^sa_2^2 + {}^ib_1^2\,{}^sb_2^2 + {}^ic_1^2\,{}^sc_2^2)\,\overline{n_1^4} $$
$$ [{}^ia_1^2({}^sb_2^2 + {}^sc_2^2) + {}^ib_1^2({}^sc_2^2 + {}^sa_2^2) + {}^ic_1^2({}^sa_2^2 + {}^sb_2^2)]\,\overline{n_2^2n_3^2} $$
$$ + 4[{}^ib_1{}^ic_1{}^sb_2{}^sc_2 + {}^ic_1{}^ia_1{}^sc_2{}^sa_2 + {}^ia_1{}^ib_1{}^sa_2{}^sb_2]\,\overline{n_2^2n_3^2}. $$

Noting that ${}^sa_2^2 + {}^sb_2^2 + {}^sc_2^2 = 1$, and making use of (52), we find

$$ \overline{{}^in_1^{2\,s}n_2^2} = ({}^ia_1^{2\,s}a_2^2 + {}^ib_1^{2\,s}b_2^2 + {}^ic_1^{2\,s}c_2^2)\,(\overline{n_1^4} - 3\overline{n_2^2n_3^2}) + (1 + 2\cos^2 \widehat{\xi_i\eta_s})\,\overline{n_2^2n_3^2}. $$

Inserting numerical values from (59), the first term of the above expression vanishes, and we are left with

$$ \overline{{}^in_1^2\,{}^sn_2^2} = \tfrac{1}{15}\{1 + 2\cos^2 \widehat{\xi_i\eta_s}\}, \qquad (60) $$

with similar expressions obtained by rotating the suffixes (1, 2, 3) as already explained.

It is obvious that for the principal directions of the ith dispersion charge the result of averaging for an isotropic distribution of molecular orientations is to give for all values of i

$$ \overline{{}^in_1^4} = \overline{{}^in_2^4} = \overline{{}^in_3^4} = \tfrac{1}{5} \quad \text{and} \quad \overline{{}^in_2^2\,{}^in_3^2} = \overline{{}^in_3^2\,{}^in_1^2} = \overline{{}^in_1^2\,{}^in_2^2} = \tfrac{1}{15} \qquad (61) $$

as may easily be verified by making use of (51). It is easily seen that with these formulæ (60) is in agreement as a particular case, since on identifying i and s we leave $\widehat{\xi_i\eta_i} = \tfrac{1}{2}\pi$, and on identifying the suffixes 1 and 2 and at the same time i and s, we have $\widehat{\xi_i\zeta_i} = 0$.

Making use of (60) and (61) we obtain finally as a result of averaging (58),

$$ \overline{K^2} = \tfrac{1}{5}\sum_i (A_i^2 + B_i^2 + C_i^2) + \tfrac{2}{15}\sum_i (B_iC_i + C_iA_i + A_iB_i) $$
$$ + \tfrac{2}{15}\sum_i\sum_s [A_iA_s + B_iB_s + C_iC_s + B_iC_s + C_iA_s + A_iB_s + B_sC_i + C_sA_i + A_sB_i] $$
$$ + \tfrac{4}{15}\sum_i\sum_s (A_iB_iC_i)(A_sB_sC_s)\cos^2(\xi_i\eta_i\zeta_i)(\xi_s\eta_s\zeta_s), $$

where the abbreviated notation of (53) is employed in the last term.

Introducing the squared value of (57) and substituting from (54) we find

$$\overline{K^2} = \tfrac{3}{5}(\overline{K})^2 + \tfrac{2}{5}(\overline{H^2} + \overline{J^2} + \overline{K^2}),$$

or remembering from (56) that $\overline{H^2} = \overline{J^2}$, we have

$$3\overline{K^2} - 4\overline{H^2} = 3(\overline{K})^2 \tag{62}$$

If, as in (26), we define ρ by the equation

$$\rho = 2\overline{H^2}/(\overline{H^2} + \overline{K^2}) \tag{63}$$

we find from (62) that

$$\overline{H^2} = \overline{J^2} = 3(\overline{K})^2 \cdot \frac{\rho}{6 - 7\rho} \quad \text{and} \quad \overline{K^2} = 3(\overline{K})^2 \cdot \frac{2-\rho}{6-7\rho}. \tag{64}$$

§ 7. *Scattering and Extinction of Light in Gases : Invariant Formulæ.*

In a gas not too near the critical point, we suppose the molecules to be sufficiently far apart that the distribution of molecular orientations is unaffected by intermolecular forces.* Owing to the rapidly changing positions of the gaseous molecules due to their high velocities, it is usually assumed that each molecule contributes to the *intensity* of the scattered radiation.† Adding the squares of the amplitudes of the vectors (P, Q, R) given in (48) for

$$\nu = n_0\overline{V} \tag{65}$$

molecules contained in a finite volume $\overline{V}$, we have

$$\left.\begin{aligned} &\Sigma\,|\,P\,|^2 = 0 \qquad \Sigma\,|\,Q\,|^2 = \frac{p^4}{c^4 r^2}|\,Z + Z_p\,|^2 \sum_1^\nu (J\cos\chi - K\sin\chi)^2 \\ &\Sigma\,|\,R\,|^2 = \frac{p^4}{c^4 r^2}|\,Z + Z_p\,|^2 \sum_1^\nu (-H\sin\theta + J\cos\theta\sin\chi + K\cos\theta\cos\chi)^2 \end{aligned}\right\} \tag{66}$$

where H, J, K have the values defined by (49).

Owing to the existence of molecular rotations, we may expect an isotropic distribution of molecular orientations. We may thus write

$$\sum_1^\nu J^2 = \nu\overline{J^2}, \qquad \sum_1^\nu K^2 = \nu\overline{K^2}, \qquad \sum_1^\nu H^2 = \nu\overline{H^2},$$

* Except, possibly, for a short interval of time at the "instant" of collision, an effect which may explain deviations from the law $(\mu-1)/\rho$=constant in gases at low pressures. Posejpal, V., "Sur la variation de la réfraction des gaz avec la pression, etc.," 'Jour. de Physique et le Radium,' vol. II, p. 85 (March, 1921).

† This point is discussed at length by Sir J. J. Thomson, 'Phil. Mag.,' vol. 40, p. 400 (1920).

and remembering that by (55) the averaged product-terms of (H, J, K) vanish,

$$\left.\begin{aligned}\Sigma\,|\,Q\,|^2 &= \frac{p^4}{c^4 r^2}\,|\,Z + Z_p\,|^2\,\nu\,(\overline{J^2}\cos^2\chi + \overline{K^2}\sin^2\chi)\\ \Sigma\,|\,R\,|^2 &= \frac{p^4}{c^4 r^2}\,|\,Z + Z_p\,|^2\,\nu\,(\overline{H^2}\sin^2\theta + \overline{J^2}\cos^2\theta\sin^2\chi + \overline{K^2}\cos^2\theta\cos^2\chi)\end{aligned}\right\}. \quad (67)$$

We proceed to consider two cases, depending on whether the incident light is polarized or unpolarized.

Case I. Incident light plane-polarized.—If we denote by I the intensity of the incident light, and by $I_s(\theta, \chi)$ that of the scattered light in a direction (θ, χ) with reference to the incident beam (fig. 2), we have, for the ratio of the scattered to the incident radiation,

$$\frac{I_s(\theta, \chi)}{I} = \frac{\Sigma\,|\,Q\,|^2 + \Sigma\,|\,R\,|^2}{|\,Z\,|^2}. \qquad (68)$$

Remembering that $\overline{H^2} = \overline{J^2}$, and making use of (65), we find after some reductions that (67) and (68) give

$$\frac{r^2 I_s(\theta, \chi)}{VI} = \frac{|\,Z + Z_p\,|^2}{|\,Z\,|^2}\frac{p^4}{c^4}\,n_0\,[\overline{H^2} + \overline{K^2} + (\overline{H^2} - \overline{K^2})\sin^2\theta\cos^2\chi]. \qquad (69)$$

Substituting for the ratio $|\,Z + Z_p\,| / |\,Z\,|$ from (37), and making use of (64), we may write (69) in the form, remembering that $p = 2\pi c/\lambda$,

$$\frac{r^2 I_s(\theta, \chi)}{VI} = \frac{\pi^2}{\lambda^4}\frac{(\mu^2 - 1)^2}{n_0}\cdot\frac{6}{6 - 7\rho}[1 - (1 - \rho)\cos^2\chi\sin^2\theta]. \qquad (70)$$

If we examine the scattered light in the direction (θ, χ) by means of a Nicol prism, we find for the *depolarization*, or ratio of minimum to maximum intensities, on rotating the prism

$$\begin{aligned}\rho(\theta, \chi) = \frac{\Sigma\,|\,R\,|^2}{\Sigma\,|\,Q\,|^2} &= \left[\frac{\overline{H^2} + \overline{K^2}\cos^2\theta}{\overline{H^2}\cos^2\chi + \overline{K^2}\sin^2\chi} - \cos^2\theta\right]\\ &= \left[\frac{\rho + (2 - \rho)\cos^2\theta}{\rho\cos^2\chi + (2 - \rho)\sin^2\chi} - \cos^2\theta\right]. \qquad (71)\end{aligned}$$

This formula is greatly simplified when the incident beam is polarized so that $\chi = \frac{1}{2}\pi$, when $\rho(\theta, \frac{1}{2}\pi) = 2/(2 - \rho)$ which is independent of θ, while for

$\chi = 0, \qquad \rho(\theta, 0) = \sin^2\theta + (2/\rho - 1)\cos^2\theta.$

Case II. Incident light unpolarized.—In almost all experimental arrangements an unpolarized incident beam is employed. By averaging the intensities given in (66) for all possible orientations χ of the plane of polarization, the

amplitude $|Z|$, and therefore $|Z + Z_p|$ remaining constant, we obtain, on replacing $\sin^2 \chi$ and $\cos^2 \chi$ by their mean values $\frac{1}{2}$,

$$\frac{r^2 I_s(\theta)}{VI} = \frac{1}{2}\frac{\pi^2}{\lambda^4}\frac{(\mu^2-1)^2}{n_0} \cdot \frac{6(1+\rho)}{6-7\rho}\left\{1+\frac{1-\rho}{1+\rho}\cos^2\theta\right\}, \tag{72}$$

while the depolarization in a direction θ with the incident beam is given by

$$\rho(\theta) = \rho + (1-\rho)\cos^2\theta. \tag{73}$$

From this formula we notice that $\rho(\frac{1}{2}\pi) = \rho$ is the depolarization when the scattered light is examined by a Nicol or double-image prism at right angles to the unpolarized incident beam.

For light scattered at right angles to the incident beam ($\theta = \frac{1}{2}\pi$) we have

$$\frac{r^2 I_s(\frac{1}{2}\pi)}{VI} = \frac{1}{2}\frac{\pi^2}{\lambda^4}\frac{(\mu^2-1)^2}{n_0} \cdot \frac{6(1+\rho)}{6-7\rho}, \tag{74}$$

which agrees with Cabannes' modification of Rayleigh's well-known formula by the introduction of the factor $6(1+\rho)/(6-7\rho)$ depending on molecular anisotropy, as a result of which observed and theoretical values of relative scattering in various dust-free gases are brought into much closer agreement.*

It does not appear to have been pointed out that molecular anisotropy results in a deviation from the well-known $(1+\cos^2\theta)$ law for relative intensities of scattered light in various directions with the incident beam. From (72) and (74) we have

$$I_s(\theta) = I_s(\tfrac{1}{2}\pi)\left\{1+\frac{1-\rho}{1+\rho}\cos^2\theta\right\}. \tag{75}$$

Owing to molecular anisotropy, Rayleigh's well-known formula for extinction of light in gaseous media as a result of scattering is sensibly modified, as, in fact, was foreseen by that writer.†

The rate of flow of energy from an element of volume $V = S\,dx$, of cross-section S and thickness dx, across an element of surface $r^2 d\omega$ subtending a small solid angle $d\omega = \sin\theta\, d\theta\, d\phi$ at the origin in a direction θ with the incident beam is, on integrating with respect to the azimuth ϕ,

$$c\int I_s(\theta)\,.\,r^2 d\omega = c\,r^2 I_s(\tfrac{1}{2}\pi)\,.\,2\pi\int_0^{\pi}\left\{1+\frac{1-\rho}{1+\rho}\cos^2\theta\right\}\sin\theta\,d\theta, \tag{76}$$

c being the velocity of light.

Since the present theory does not take into account any dissipation of energy by individual molecules, the rate of flow of energy expressed in (76) is equal to

* Cabannes, J., 'Annales de Physique,' vol. 15, p. 130 (1921).

† Lord Rayleigh, 'Scientific Papers,' vol. VI., p. 546.

the rate of loss of energy from the incident beam of cross-section S on travelling a distance dx, *i.e.*

$$-c\,\mathrm{S}d\mathrm{I} = c\mathrm{S}\kappa\mathrm{I}dx \tag{77}$$

where κ is the coefficient of extinction defined by the relation

$$d\mathrm{I}/dx = -\kappa\mathrm{I}.$$

On equating (76) and (77), integrating the latter and making use of (74) with $\mathrm{V} = \mathrm{S}dx$, we find for the coefficient of attenuation the expression—

$$\kappa = \frac{8\pi^3}{3\lambda^4}\frac{(\mu^2-1)^2}{n_0}\cdot\frac{6+3\rho}{6-7\rho}. \tag{78}$$

It is interesting to note that the formulae (71), (72), (74) and (78) have been derived for a very general type of molecule, and that these results, involving experimentally observed quantities are *invariant* with respect to such details of molecular constitution as number and magnitude of dispersion charges, their position and the mutual orientation of their principal directions.

Although the results thus far obtained have been based on a general type of "static" molecule, the theory is by no means opposed to the modern conceptions of the "dynamic" atom. For wave-lengths long compared to molecular dimensions, we may suppose those perturbations which contribute principally to dispersion to consist of forced oscillations of each atomic system of electrons with respect to the corresponding positive system.

§ 8. *Scattering and Extinction of Light in Gaseous Mixtures.*

(i) *Theory.*—Consider a mixture of r different kinds of molecules, there being n_r per unit volume of each. As in § 5 (ii), we denote for each constituent, the molecular density by N_r, the molecular weight by m_r and the mass-density by D_r. If w_r is the weight of each constituent per unit volume of mixture of density D, we have

$$w_r = m_r n_r, \qquad \mathrm{D} = \sum_r w_r, \qquad n_r/\mathrm{N}_r = w_r/\mathrm{D}_r, \tag{79}$$

and the proportion τ_r of each constituent by weight is given by

$$\tau_r = w_r/\mathrm{D}. \tag{80}$$

As in the preceding section, we shall suppose that each molecule contributes independently to the *intensity* of the scattered light. Limiting ourselves to the case of *unpolarized incident light*, for which $\overline{\cos^2\chi} = \overline{\sin^2\chi} = \frac{1}{2}$, we have for the light scattered by $\Sigma n_r\mathrm{V}$ molecules contained in a volume V, from equation (67)

$$\left.\begin{aligned}\Sigma\,|\,Q\,|^2 &= \tfrac{1}{2}\frac{p^4V}{c^4r^2}\,|\,Z+Z_p\,|^2\sum_r n_r\,[\overline{H_r^2}+\overline{K_r^2}]\\ \Sigma\,|\,R\,|^2 &= \tfrac{1}{2}\frac{p^4V}{c^4r^2}\,|\,Z+Z_p\,|^2\sum_r n_r\,[2\overline{H_r^2}+(\overline{K_r^2}-\overline{H_r^2})\cos^2\theta],\end{aligned}\right\} \tag{81}$$

in which $\overline{H_r^2}$ and $\overline{K_r^2}$ refer to expressions of the form (49) for the r^{th} type of complex anisotropic molecule averaged for all possible independent molecular orientations.

Z_p refers to the polarization field of the medium made up of the r types of molecules. If it has been ascertained experimentally that Lorentz's additive law (46)

$$\frac{1}{D}\frac{\mu^2-1}{\mu^2+2}=\sum_r\frac{\tau_r}{D_r}\frac{\mu_r^2-1}{\mu_r^2+2} \tag{82}$$

is obeyed to a sufficient degree of accuracy, we conclude that S_r is negligibly small for each constituent, and therefore from (39) we have—

$$|\,Z+Z_p\,|\,/\,|\,Z\,|=\tfrac{1}{3}(\mu^2+2). \tag{83}$$

It follows from (81) that the intensity scattered in the direction θ is given by

$$\begin{aligned}\frac{r^2I_s(\theta)}{VI}&=\frac{r^2}{V}\cdot\frac{\Sigma\,|\,Q\,|^2+\Sigma\,|\,R\,|^2}{Z^2}\\ &=\tfrac{1}{2}\frac{p^4}{c^4}\left(\frac{\mu^2+2}{3}\right)^2\sum_r n_r\,[(3\overline{H_r^2}+\overline{K_r^2})+(\overline{K_r^2}-\overline{H_r^2})\cos^2\theta].\end{aligned} \tag{84}$$

If we consider that the r^{th} constituent alone is present in the volume V, we write $n_r=0$ for all types of molecules except the r^{th}, when $n_r=N_r$. If examined under the same conditions as the mixture (r, θ and I being the same), we have

$$\frac{r^2\,{}^rI_s(\theta)}{VI}=\tfrac{1}{2}\frac{p^4}{c^4}\left(\frac{\mu_r^2+2}{3}\right)^2.\,N_r\,[(3\overline{H_r^2}+\overline{K_r^2})+(\overline{K_r^2}-\overline{H_r^2})\cos^2\theta].$$

Substituting in (84), and making use of (79) and (80), we obtain an additive law for the intensity of scattered light in the form

$$\frac{1}{D}\frac{I_s(\theta)}{(\mu^2+2)^2}=\sum_r\frac{\tau_r}{D_r}\frac{{}^rI_s(\theta)}{(\mu_r^2+2)^2}. \tag{85}$$

If κ is the coefficient of extinction by scattering for the mixture, and k_r that of the r^{th} constituent for density D_r, we see on integrating (85) over a sphere of large radius to obtain the rate of flow of energy from an element of volume of unit cross-section and thickness dx, that the corresponding additive law is

$$\frac{1}{D}\frac{\kappa}{(\mu^2+2)^2}=\sum_r\frac{\tau_r}{D_r}\frac{k_r}{(\mu_r+2)^2}. \tag{86}$$

The *depolarization* of the mixture at right angles to the incident beam is given by writing $\theta = \frac{1}{2}\pi$ in (81). We then have

$$\rho = \frac{\Sigma\,|\,R^2\,|}{\Sigma\,|\,Q\,|^2} = \frac{2\sum_r n_r \overline{H_r^2}}{\sum_r n_r\,(\overline{H_r^2} + \overline{K_r^2})}$$

Making use of (64) for each constituent and (42), we easily derive the result given below for mixtures for which Lorentz's additive law (82) holds,

$$\frac{\rho}{6-7\rho} = \frac{\sum_r n_r M_r^2 \rho_r/(6-7\rho_r)}{\sum_r n_r M_r^2} = \frac{\sum_r \frac{v_r}{N_r} \cdot \left(\frac{\mu_r^2-1}{\mu_r^2+2}\right)^2 \cdot \frac{\rho_r}{6-7\rho_r}}{\sum_r \frac{v_r}{N_r} \cdot \left(\frac{\mu_r^2-1}{\mu_r^2+2}\right)^2}, \qquad (87)$$

where M_r is the molecular refractivity of the constituent r as defined by (41) and v_r the volume of the constituent r per unit volume of mixture given by

$$v_r = w_r/D_r = n_r/N_r. \qquad (88)$$

These formulae have been derived without approximation, so that the hypothesis of molecular independence, as regards orientation and contribution to intensity of the scattered light, may be tested out by comparison with experiments on gases under high pressures, on saturated vapours and on liquids.

(ii) *Application to atmospheric extinction.*—In view of the fact that the extinction coefficient of the earth's atmosphere is accurately known for various wave-lengths over the range of the visible spectrum,* and provides an accurate means of computing the molecular density of gases at 0° and 760 mm. pressure,† it is of considerable importance to investigate the effect of molecular anisotropy which enters into the expression for the extinction coefficient as shown by (78). Referring refractive indices and extinction coefficients to 0° and 760 mm., we may without sensible error replace (μ_r^2+2) by 3 in (86). In these circumstances, the molecular density of each constituent by itself is constant for all gases, *i.e.* $N_r = n_0$, and by (80) and (88) we may write—

$$\kappa = \sum_r \frac{n_r}{n_0}\,\kappa_r = \sum_r v_r\,\kappa_r, \qquad (89)$$

where v_r is the proportion by volume of each constituent.

For gaseous media we have, approximately,

$$\kappa_r = \frac{32}{3}\,\frac{\pi^3}{\lambda^4}\,\frac{(\mu_r-1)^2}{n_0} \cdot \frac{6+3\rho_r}{6-7\rho_r}. \qquad (90)$$

* 'Annals of the Smithsonian Astrophysical Observatory,' Washington, vols. III (1913) and IV (1922).

† King, L. V., 'Nature,' vol. 93, p. 557 (1914). Fowle, F. E., 'Astrophysical Jour.,' vol. 40, p. 435 (1914).

If air be considered as an aggregate of symmetrical molecules of refractive index μ_a, the molecular density n_a has hitherto been calculated from the uncorrected formula—

$$k = \frac{32}{3}\frac{\pi^3}{\lambda^4 n_a}(\mu_a - 1)^2.$$

Comparing this with (98) we see that—

$$n_0/n_a = \sum_r v_r \left(\frac{\mu_r - 1}{\mu_a - 1}\right)^2 \cdot \frac{6+3\rho_r}{6-7\rho_r}, \tag{91}$$

the right hand side representing the factor by which the uncorrected value n_a must be multiplied to give the correct value of n_0.

Considering the three principal components of the atmosphere, we have the following data :—

Table I.

	Oxygen.	Nitrogen.	Argon.	Air.	Remarks.
v_r	0·210	0·781	0·009	1·000	
$(\mu_r - 1)$	$27 \cdot 2 \times 10^{-5}$	$30 \cdot 0 \times 10^{-5}$	$28 \cdot 4 \times 10^{-5}$	$29 \cdot 5 \times 10^{-5}$	$\lambda = 4600$ Å.
ρ_r	0·094	0·0406	0·032	0·050	Rayleigh,* white light.

From this data we obtain $n_0 = n_a \times 1 \cdot 084$. If we make use of Cabannes' determinations of depolarization, *i.e.* 0·054 for oxygen, 0·028 for nitrogen, and 0·00 for argon, formula (91) gives 1·049 for this correction factor.†

A further correction arises from the fact that in the outer atmosphere, in isothermal equilibrium, the relative molecular density of the rth constituent depends on the molecular weight according to the formula‡

$$\log(n_r/n_{r0}) = -m_r gz/(\mathrm{RT}) \tag{92}$$

in which the curvature of the earth is neglected. In this equation, n_{r0} is the molecular density at the lower boundary of the outer atmosphere from which the height z is also measured.

In computing the extinction of light by the earth's atmosphere, it is necessary

* Lord Rayleigh, 'Roy. Soc. Proc.,' vol. 94, A, p. 453 (1918).

† Cabannes ('Annales de Physique,' vol. 15, p. 30 (1921)) inadvertently assumes that $I_s(\theta) = (1+\cos^2\theta)\, I_s(\frac{1}{2}\pi)$ instead of (84) and derives $(6+6\rho)/(6-7\rho)$ as the factor by which the coefficient of extinction is affected by molecular anisotropy, instead of the correct value given in (87). Using his own values for the depolarization quoted above, he obtains 1·07 for the correction factor, and from independent observations on relative scattering, the value 1·10. He concludes, finally, that Fowle's estimate of $n = 2 \cdot 69 \times 10^{19}$ should be increased to $2 \cdot 92 \times 10^{19}$.

‡ Jeans, 'The Dynamical Theory of Gases,' 2nd Edition, p. 351 (1916).

to take into account the variable proportion of oxygen and nitrogen in the formulæ (89) and (90) for mixtures as far as the stratosphere ($p = \frac{1}{4}p_0$). Within the stratosphere, to the level considered, the relative proportions of the constituent gases remain the same owing to convection. The further consideration of this interesting question must, however, be left to a future paper.

With regard to experimental evidence on the constitution of the extreme limits of the upper atmosphere, it may be pointed out that observations on the depolarization of the zenith sky after sunset may, on comparison with values for gaseous mixtures computed from laboratory data, enable us to test the isothermal theory.*

(iii) *Test of Theory of Scattering in Gaseous Mixtures.*—When pressure and temperature are far removed from the critical values of any constituent, we may write $N_r = n_0$, and replace μ_r^2+2 by 3. In these circumstances, the additive law (85) becomes—

$$I_s(\theta) = \sum_r v_r {}^r I_s(\theta), \tag{93}$$

while the depolarization of the mixture, given by (87), becomes—

$$\frac{\rho}{6-7\rho} = \frac{\sum_r v_r \dfrac{\rho_r(\mu_r-1)^2}{6-7\rho_r}}{\sum_r v_r(\mu_r-1)^2}. \tag{94}$$

As far as the writer is aware, no observations have as yet been carried out for the special purpose of testing the laws of scattering and depolarization in gaseous mixtures, and such are greatly to be desired.

We may, however, test formula (94) by computing the depolarization of air in terms of that of its two most important constituents, oxygen and nitrogen, making use of the data of Table I. We easily find $\rho = 0 \cdot 0505$ (calculated), in good agreement with $\rho = 0 \cdot 050$ (observed). This satisfactory agreement goes far to justify the hypothesis of molecular independence assumed by the theory.†

Further observations over a wide range of pressures and temperatures are greatly to be desired, especially in gases capable of chemical combination, and in gases near the critical point. The depolarization is very sensitive to intermolecular influence as affecting complete independence of molecular orientations.

* Fabry, C., "Remarques sur la diffusion de la lumière par les gaz," 'Jour. de Physique,' vol. VII, pp. 89–102 (1917). Raman, C. V., 'Molecular Diffraction of Light' (University of Calcutta Press, 1922).

† According to Cabanne's determinations, $\rho_1 = 0 \cdot 054$ for oxygen and $\rho_2 = 0 \cdot 028$ for nitrogen. Formula (94) gives for air $\rho = 0 \cdot 034$ (calculated) to be compared with $\rho = 0 \cdot 040$ (observed). The agreement is not so satisfactory in this case.

The same remark applies to the effect on depolarization of molecular aggregation, which, even in the case of a single gas, may be expected to give rise to an observable effect as the critical point is approached. Observations on light scattering in vapours in contact with their liquids would give some indications of molecular aggregation, and of circumstances of molecular collisions which determine peculiarities in the experimentally determined equation of state not interpretable in terms of the dynamical theory of gases.

Summary and Conclusions.

Observations by Cabannes, the present Lord Rayleigh, Gans and others have shown that the light scattered by various gases in a direction at right angles to the incident beam is not completely polarized. This is accounted for by Cabannes on the theory of the *simple anisotropic molecule* as developed by Langevin in 1910 to account for electric and magnetic double refraction. Such a molecule contains a single dispersion electron acted on by unequal quasi-elastic restoring forces along *three principal directions* and capable of vibrating with three different frequencies.

The present writer has extended the theory to gaseous and liquid media composed of *complex anisotropic molecules*, in which there are any number of dispersion charges, not necessarily equal, whose principal directions of vibration are not parallel.

For an isotropic medium in which all molecular orientations are equally probable, a general dispersion formula of the Lorentz type is derived.

In gaseous media, owing to continual changes of position, each molecule contributes independently to the *intensity* of the scattered radiation. For unpolarized incident light of intensity I, the depolarization ρ is the ratio of the minimum to maximum intensity when the light scattered at right angles is examined by a Nicol prism, and, as observed in gases, is a quantity characteristic of the molecule. The intensity $I_s(\theta)$ of light of wave-length λ scattered in a direction θ with the incident beam to a distance r from a volume V is given by the formula—

$$\frac{r^2 I_s(\theta)}{\mathrm{VI}} = \tfrac{1}{2}\,\frac{\pi^2}{\lambda^4}\,\frac{(\mu^2-1)^2}{n}\cdot\frac{6(1+\rho)}{6-7\rho}\left\{1+\frac{1-\rho}{1+\rho}\cos^2\theta\right\}, \tag{95}$$

where μ is the refractive index of the medium corresponding to molecular density n.

The corresponding expression for the coefficient of extinction by scattering is—

$$\kappa = \frac{8\pi^3}{3\lambda^4}\,\frac{(\mu^2-1)^2}{n}\cdot\frac{6+3\rho}{6-7\rho}. \tag{96}$$

A remarkable feature of these formulæ is their *invariance* with respect to such details of molecular structure as number and magnitude of dispersion charges, their position, and the mutual orientation of their principal directions.

Formulæ of the same invariant character are derived for scattering, depolarization and extinction of light in gaseous mixtures. In particular, the depolarization of air calculated in terms of that of its principal constituents, oxygen and nitrogen, is in good agreement with observation, making use of the present Lord Rayleigh's data. An important application of these formulae lies in the re-determination of Avogadro's constant from observations on the extinction of solar radiation by the earth's atmosphere, correcting for molecular anisotropy and the probable variation in the proportions of its constituent gases above the stratosphere.

An invariant formula analogous to (95), based on Smoluchouski's theory of fluctuations of density, has been obtained for the scattering of light by dust-free liquids, and is in satisfactory agreement with Martin's observations. This phase of the subject the writer hopes to deal with in a future paper.

The Molecular Scattering of Light in Carbon Dioxide at High Pressures.

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(Communicated by Dr. G. T. Walker, F.R.S.—Received June 7, 1923.)

1. *Introduction.*

The investigation described in this paper was undertaken in order to test theories of light-scattering by quantitative observations on carbon dioxide, under pressures ranging from 1 to 100 atmospheres, and temperatures from 0° C. to 50° C. The work includes a study of the following cases :—(1) the scattering of light by the unsaturated vapour ; (2) by the saturated vapour in thermal equilibrium with the liquid ; (3) by the liquid under the pressure of its own vapour ; (4) by the liquid under impressed pressure higher than the vapour tension ; (5) by the substance in the vicinity of the critical state ; and (6) by the substance in the gaseous state above the critical temperature.*

* The cases in which the fluid is superheated or supercooled and is in metastable equilibrium are not dealt with here.

Carbon-dioxide was chosen as a suitable substance for a comprehensive study of this kind for several reasons. The fact that it can be obtained commercially in cylinders in a practically pure condition greatly simplifies the experimental technique, and any pressure within the limits mentioned can be obtained without the use of special compressors. Then, again, the necessary pressure-volume data for the vapour and the gas are available from the work of Amagat* and for the liquid from that of Jenkin,† and the variation of its refractive index with density has also been fully studied by various investigators, notably by Phillips.‡ The existence of these data makes a theoretical calculation of the light-scattering possible. Further, carbon dioxide at atmospheric pressure shows a marked imperfection in the polarisation of the transversely scattered light, the ratio of the weak to the strong component of polarisation in the visual region of the spectrum being 10·6 per cent. Hence, it is a very convenient substance for studying the effect of variations of temperature and pressure on the state of polarisation of the scattered light.

Another reason why we felt impelled to take up a careful study of the scattering of light in carbon dioxide was that certain results obtained by Lord Rayleigh with this gas§ were, as has already been pointed out by us,|| anomalous and stood in need of explanation. Rayleigh determined the intensity of the light scattered by carbon dioxide vapour contained in a steel cross-tube provided with glass windows and kept in communication with a steel cylinder containing liquid CO_2 at 21° C. He found the scattering to be 102 times stronger than that of CO_2 at atmospheric pressure and inferred that the scattering power was proportional to the density within the limits of experimental error. According to the Einstein-Smoluchowski formula, however, the scattering power should have been much larger, about 800 times that of CO_2 at atmospheric pressure.

With regard to this discrepancy, it should be mentioned that Rayleigh's assumption that the density of the gas in his observation tube was equal to that of the saturated vapour at 21° C., is open to question. It is mentioned in his paper that the observation tube was leaky, and that a gauge in the communication tube from the supply cylinder indicated only 50 atmospheres, while according to the measurements of Andrews the saturation

* Amagat, 'Ann. Chem. Phys.,' (6), vol. 29, p. 52 (1893).

† Jenkin, 'Proc. Roy. Soc.,' A, vol. 98, p. 170.

‡ Phillips, 'Proc. Roy. Soc.,' A, vol. 97, p. 225.

§ Lord Rayleigh, 'Proc. Roy. Soc.,' A, vol. 95, p. 155.

|| 'Molecular Diffraction of Light' (Calcutta University Press), p. 61 (1922); also Phil. Mag.,' Jan., p. 113 (1923).

pressure at 21° C. is 60 atmospheres. From the diagram given in Rayleigh's paper, it is noticed that after passing the pressure gauge the gas had to filter through a steel tube tightly packed with cotton-wool, which must have greatly impeded the inflow of the gas into the observation tube to replace that lost by leakage, and hence the density of the gas whose scattering power was measured was in all probability considerably less than that of the saturated vapour. If we assume that the pressure in the observation tube was somewhat less than that shown by the gauge and was, say, 45 atmospheres, the scattering power, if it were proportional to the density, would only have been about 60 times that of CO_2 at atmospheric pressure at the same temperature, while according to the Einstein-Smoluchowski theory of scattering, it would be about 125 times. The experimental result,. rightly interpreted, thus tends to support the Einstein law of scattering, and not the Rayleigh law. The matter, however, appeared sufficiently important to justify a careful re-examination, with apparatus so designed that no uncertainty as to the actual density of the vapour arises.

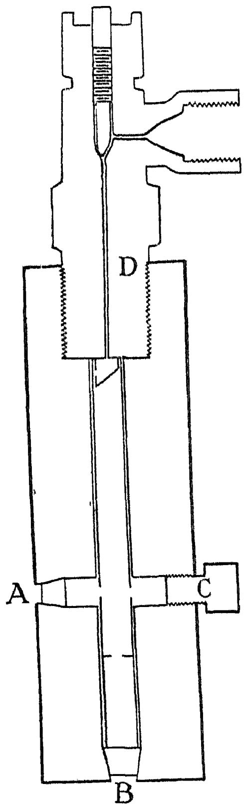
2. *Experimental Arrangements.*

In the present investigation, two distinct series of observations were made. In the first set, the scattering medium was CO_2 (vapour or liquid as the case may be) enclosed in sealed glass bulbs, thus avoiding all uncertainty regarding the density of the fluid used. A spherical bulb a little over 1 cm. in diameter was blown at one end of a stout walled capillary tube with rather a wide bore. The tube was carefully dried and exhausted, and dry CO_2 was introduced into it while immersed in liquid air. When the requisite quantity of carbon dioxide snow had condensed, the tube was sealed off leaving about 5 cm. attached to the bulb as a stem. Separate bulbs were prepared for the liquid and the vapour containing respectively an excess of the liquid and of the vapour. To prevent the bulbs bursting when the temperature is raised, sufficient volume for expansion is allowed in the stems attached to them. On removal from the liquid air, the carbon dioxide liquefies under the pressure.

The bulb and attached stem are completely blackened over with paint except for two tiny windows, one on either side of the bulb, for entry and exit of a narrow but powerful pencil of sunlight, and an aperture at the base of the bulb for observation of the scattered light. The stem with its bore forms a black cave against which the track of the beam through the CO_2 liquid or vapour, as the case may be, can be conspicuously observed. The bulb is completely immersed inside a water-bath with plate-glass slides, the rear-

walls being blackened so as to provide a dark field for observation. The temperature of the bath is regulated by adding either lumps of ice or hot water as desired. The brightness of the track of light is compared with that in another sealed tube containing a suitable dust-free liquid, like ether or benzene, or in a slab of optical glass, which serves as a standard and is also immersed in the bath, the same pencil of light passing through both. A rotating sector photometer with double disc placed in front of the cell enables the visual intensities of the two tracks to be equalised and their ratio thus to be determined.

Sealed bulbs, while convenient in many ways, are rather unsatisfactory optically when feeble light-scattering has to be measured, owing to the unavoidable reflections from the walls of the small-sized bulbs, which alone can sustain the high pressures. They are, therefore, not suitable for unsaturated vapours. It is also not possible with bulbs to work at pressures higher than the vapour-tension at the given temperature. Further, owing to the convergence of the light by the spherical walls, errors are also introduced in the photometry. In order to avoid these difficulties, in the second series of experiments, the simple form of apparatus shown was developed by the authors. This can safely withstand very high pressures and is suitable for the study of light-scattering in gases and liquids.



The observation tube consisted of a massive solid steel cylinder, 20 cm. long and 6·5 cm. in diameter, in which were drilled two cylindrical conical-ended holes, A and B, one axial and the other diametral. Two thick glass windows were ground in at A and B, the former to admit the primary beam of light and the latter for the observation of the scattered track. After the glass windows had been ground in, a tube with apertures for the entry of the primary beam and observation of the scattered light was put in place within the steel cylinder. This tube and the steel cylinder were enamelled black, a pin-valve was fitted to the end D, and the opening at C was closed up. To secure a good black background, a plate of black glass was fitted at an

angle of 45° inside the cylinder as shown. The observation tube could be connected to a pressure gauge and to the supply cylinder containing CO_2. Stopcocks placed on either side of the pressure gauge served to cut off its connection either with the observation tube or the supply cylinder as desired.

That the readings of pressure given by the gauge were reliable was tested in the following manner. The observation cylinder was *partly* filled with liquid and kept in communication with the gauge, the connection with the supply cylinder being cut off. The readings of the gauge were taken corresponding to different temperatures of the observation cylinder and were found to agree with the saturation pressures at those temperatures given by Amagat. The supply cylinder (which had been tested to stand 200 atmospheres) was placed in a vessel containing water, and by adjustment of the temperature of the water, pressures up to 100 atmospheres could be reached. The observation tube was placed in a rectangular glass vessel containing water, and its temperature could be kept constant at any desired value between 5° C. and 50° C. The observation cylinder and connecting tubes were evacuated before admission of carbon dioxide. The evacuation and re-admission of CO_2 were repeated until the track appeared a good blue with no evidence of dust particles.

For measurements of the scattering in saturated vapour, a shallow layer of liquid was allowed to condense at the bottom of the observation cylinder and the pin-valve at D closed. After a sufficient time had elapsed for the attainment of equilibrium, the intensity of the scattered light was compared with that in a standard substance as usual. For observations in the liquid in equilibrium with the vapour, the liquid was allowed to fill up more than three-fourths of the observation cylinder. The measurements of the scattering power in these two cases gave results in conformity with those obtained with the sealed bulbs.

3. *Experimental Results: Intensity of Scattering.*

(*a*) *Unsaturated Vapour.*—For experiments on unsaturated vapour, the steel observation tube was cut off from the supply cylinder, and by blowing off gas through an auxiliary outlet, any desired pressure below that of saturation could be got. The following table gives the intensity of scattering at different pressures at 30° C. in terms of the scattering of CO_2 at 0° C. and 76 cm. pressure.

Table I.

Pressure in atmospheres.	Density / Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
15	14·5	13·5	17·2	21·3	22
20	20·0	18·7	23·4	29·0	33
30	32·1	23·0	49	59	54
40	47	29·4	65·2	77	83
50	64·5	31·5	123	144	140
55	75·7	30·2	180	207	197
60	89·7	27·9	276	315	307
65	109	22·9	514	576	665
68	127	19·1	847	940	1078

It will be noted from columns 2 and 6 that the observed scattering is much larger than in proportion to the density. The values in column 4 are calculated according to Einstein-Smoluchowski formula. When the molecules are anisotropic there is an extra scattering, the "orientation scattering," whose magnitude depends on the properties of the molecule and on the state of aggregation of the fluid. Its value has been worked out in a recent paper,* and the total intensity at a distance d of the light transversely scattered by a unit volume of the fluid in any condition is given by

$$\frac{\mathrm{I}_0}{d^2}\left[\frac{\pi^2}{18}\frac{\mathrm{RT}\beta}{\mathrm{N}\lambda^4}(\mu^2-1)^2\,(\mu^2+2)^2+\frac{\pi^2}{2n_0\lambda^4}(\mu^2-1)^2\frac{r_1(9+4\gamma)}{6-7r_1}\right],$$

where n_0 is the number of molecules per unit volume in the fluid, r_1 is the ratio of the weak component to the strong in the light transversely scattered by the substance in the state of vapour at very low pressures, and γ denotes $\frac{\mathrm{RT}\beta}{\mathrm{N}}n_0\left(\frac{\mu^2+2}{3}\right)^2$. The other symbols have their usual meanings. The total scattering given by this formula is given in column 5 for comparison with the observed intensity of scattering given in column 6. The agreement is good except in the vicinity of the critical temperature, where uncertainties in temperature and impurities in the substance have a very great effect.

* K. R. Ramanathan, 'Proc. Ind. Assoc. for the Cultivation of Science,' vol. viii, pp. 1-22 (1923).

Table II.

(*b*) *Saturated Vapour.*—

Temperature.	Density / Density at N.T.P.	Reciprocal of compressibility.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
0°	48	20·6	92	106		
5°	57	21·5	120	140	102	Bulb.
10°	68	21·9	180	205	195	,,
15°	80	21·0	300	340	347	,,
20°	96	19·7	560	620	567	,,
24°	112	16·0	920	1000	1010	,,
					1050	Cylinder.
25°	121	15·0	970	1067	1190	Bulb.
26°	126	13·7	1210	1330	1920	,,
					1860	Cylinder.
28°	140	10·0	2010	2190	3630	Bulb.
					3490	Cylinder.
30°	169	5·9 (?)	5100	5500	8000	Bulb.

Table III.

(*c*) *Liquid in Equilibrium with Vapour.*—

Temperature.	Density. / Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
5°	448	700	380	494	360	Bulb.
10°	432	530	480	600	463	,,
					500	Cylinder.
15°	411	372	618	760	630	Bulb.
					730	Cylinder.
20°	387	220	905	1086	980	Bulb.
					1000	Cylinder.
23°	369	146	1240	1450	1280	,,
25°	355	110	1540	1786	1880	Bulb.
27°	340	65	2340	2620	2950	,,
29°	317	25	5080	5590	6200	,,
30°	302	15	7500	8350	11000	,,
31°	271	4	28700	31000	35000	,,

The compressibilities at temperatures higher than 20° were obtained in the following way. The reciprocals of the compressibility at the saturation points at temperatures below 20° C. (taken from Jenkin's paper) were plotted against the temperature, and taking the reciprocal of the compressibility at the critical point to be zero, a smooth curve was drawn through these points.

Table IV.

(*d*) *Liquid CO_2 at Higher Pressures.*—

Tem-perature.	Pressure in atmospheres.	Density. / Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.	Remarks.
15°	51	416	387	618	760	663	
	68	430	567	458	575	522	
	76	436	674	374	482	470	
	82	440	773	354	464	428	
25°	Saturation.	355	110	1540	1786	2100	
	68	373	195	976	1122	1650	
	74	383	243	827	968	1200	
	83	397	309	678	834	778	
	92	407	486	483	599	600	
30·5°	Saturation	289	10	10400	11300	22500	
	72·5	314	35	3600	3900	5480	These calculated values refer to 30° C.
	76·5	343	83	1880	2106	2610	
	84·0	366	155	1185	1351	1097	
	86·5	372	179	1063	1220	940	

(*e*) *Scattering above the Critical Temperature.*—

Table V.—(i) Scattering at 35° at different pressures.

Pressures in atmospheres.	Density / Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
61	85	33·5	220	253	290
67	104	27·6	401	453	680
72	125	21·2	780	866	1170
77·5	177	13·3	2580	2830	3200
81	275	13·8	5170	5220	4230
87	330	72·1	2010	2250	1750
91					1430

Table VI.—(ii) Scattering at constant density (0·320 gm./cc.) at different temperatures above the critical temperature.

Temperature.	Density / Density at N.T.P.	Reciprocal of compressibility in atmospheres.	Density scattering (Einstein formula).	Density scattering corrected for anisotropy.	Observed scattering.
32°	165	8·4	3420	3730	4550
35°	165	14·1	2060	2266	2730
40°	165	19	1550	1705	1620
50°	165	22	1380	1520	1410

4. *Polarisation of the Scattered Light: Theory and Experimental Results.*

In previous papers,* the authors have discussed the influence of the physical condition of the substance on the imperfection of polarisation of the transversely scattered light. An exact investigation of the problem has been worked out† on the assumption of anisotropic molecules with three principal axes. It leads to the formula

$$r = \frac{2f}{f+\gamma g},$$

where r is the ratio of the weak component to the strong in the transversely scattered light, and γ has the meaning already indicated in the previous section. When the substance is in the gaseous state at low pressure and Boyle's law holds good, $\gamma = 1$ and r assumes the value $2f/(f+g)$ which has been already denoted by r_1.

Also
$$g - \frac{4}{3}f = \frac{9}{16\pi^2 n_0^2}\left(\frac{\mu^2-1}{\mu^2+2}\right)^2.$$

The formula indicates that when the scattering is very large, *e.g.* in the neighbourhood of the critical point, it is almost completely polarised ; while in other cases, *e.g.* when the substance is in the liquid state much below the critical temperature, the polarisation is markedly less perfect than in the scattering by the vapour at low pressures. While these indications of theory are in qualitative agreement with facts, it is found that in the case of many liquids, there are considerable differences between theory and observation in the quantitative data, indicating that the assumption of a random orientation of the molecules made in the theory is not generally valid. This makes it all the more important that as many different substances as possible should be examined.

The problem of determining accurately the state of polarisation of light scattered by a fluid under high pressures is not without serious experimental difficulties. The principal source of error is the unavoidable strain and consequent ælotropy of the glass walls or the glass window through which the scattered light is observed. If the strain were perfectly symmetrical about the direction of observation no error would arise, but this condition is not easy to secure, especially when a conical glass window has to be pressed home into a metal recess provided for it to make it perfectly leak-tight. Small sealed bulbs are also not quite suitable in this type of work, owing to the very

* C. V. Raman and K. Seshagiri Rao, 'Phil. Mag.,' vol. 45, p. 625. K. R. Ramanathan, *loc. cit.*

† K. R. Ramanathan, *loc. cit.*

imperfect background which they furnish for observing the fainter component of polarisation. In view, however, of the fact that even an approximate determination of the state of polarisation under different conditions would be of interest, attempts were made to measure the effect with the apparatus used by the authors. The vapour or liquid inside the chamber was illuminated by a narrow horizontal beam of sunlight and on examination with a double-image prism set so as to transmit vertical and horizontal vibration, it was found that even near the critical point both images were bright, but that across the weaker one there was an intense black band running obliquely. The glass window was obviously under strain, but by isolating the portion of the glass wall transmitting the central portion of the black band alone by means of a narrow slit (nearly 1 mm. wide) placed in contact with the window, measurements of polarisation were made as usual with a double-image prism and nicol.

The following tables contain a summary of the results.

5. *Imperfection of Polarisation.*

Table VII.

(i) *Unsaturated Vapour at* 30° C.

Pressure in atmospheres.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
	Observed.	Calculated.
	Per cent.	Per cent.
30	9	8
40	8	6
50	6	4·9
60	4·5	3·1
65	4	2

(ii) *Saturated Vapour.*

Temperature.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$	
	Observed.	Calculated.
15°	5·8	2·6
20°	4	2·1
25°	3	1·2
30°	1·5	0·3

iii) *Liquid in Equilibrium with Vapour.*

Temperature.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$ Observed.	Calculated.
10°	14	10·5
15°	10	7
20°	8	6
25°	5	3·8
28°	3	1·4

(iv) *Liquid under Higher Pressures.*

Temperature.	Pressure in atmospheres.	Ratio : $\frac{\text{Weak component}}{\text{Strong component}}$ Observed.	Calculated.
20°	92	13	14
	80	10	9
25°	90	9	8

The observed values are uniformly a little too high. This is probably due to the fact that the slit used has a finite width, and transmits light to a small distance on either side of the centre of the black band. The actual course of values, however, follows the indications of theory.

6. *Summary and Conclusion.*

The paper describes a simple form of apparatus which enables the intensity and state of polarisation of the light scattered by gases and liquids at high pressures to be measured. Results obtained with carbon dioxide are given, the noteworthy features being the following :—

(1) The scattering in carbon dioxide in the condition of unsaturated vapour below the critical temperature is not proportional to the density, but increases much more rapidly as the saturation pressure is approached, and the polarisation of the transversely scattered light becomes sensibly more and more *perfect.*

(2) The scattering in the saturated vapour and in the liquid phase in equilibrium with it has also been studied. When the liquid is further com-

pressed by application of pressure in excess of the vapour tension, its light-scattering power shows a striking diminution, and the polarisation becomes markedly more *imperfect*.

(3) Above the critical temperature, the scattering power at first increases with rise of pressure, reaches a maximum, and diminishes again.

(4) Except very close to the critical temperature, the experimental results agree well with the Einstein-Smoluchowski theory of scattering when the effect of molecular ælotropy is taken into account.

We have, in conclusion, to express our cordial thanks to Messrs. The Lightfoot Refrigeration Company, of Calcutta, who gave us much assistance in fitting up the high-pressure apparatus and in other ways.

The Carbon Arc Spectrum in the Extreme Ultra-Violet.—II.

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(Communicated by Prof. A. W. Porter, F.R.S. Received July 31, 1923.)

1. *Introduction.*

In a recent paper* I have given measurements of some lines in the carbon arc spectrum in the Lyman region which had not previously been photographed. Further work has enabled me to photograph many more lines in this spectrum, and to record shorter wave-lengths in an arc spectrum than any previous worker with this source.

2. *Experimental.*

The apparatus used was precisely similar to that described in the previous paper, except in respect of the grating. Several fresh gratings have been tried, including some ruled at Johns Hopkins University and others ruled on the Blythswood engine at the National Physical Laboratory. It was with one of the latter alone that it was possible to record any lines of shorter wave-length than those given in the previous paper, and with this grating the measure-

* 'Roy. Soc. Proc.,' A, vol. 102, pp. 484–496 (1922).

ments were made. It was ruled on a 7 cms.-plate of 100 cms. radius of curvature, with a ruled area of 5·0 cms. × 3·6 cms., and had 568 lines per millimetre. The ruling was done with a very light pressure, so that as judged in the visible spectrum the central image was considerably brighter than any order of spectrum. It was, in this respect, like that described by Millikan* as giving the best results. The procedure for obtaining and estimating the vacuum was exactly as described in the previous paper, so that the extension of spectrum here recorded is not due to the attainment of a higher vacuum than that previously used.

The grating was so adjusted that the central-slit image was focussed about 1 mm. from the left-hand end of the photographic plate when the left-hand slit was illuminated. In this position the bright line at 903·7 A was photographed near to the right-hand end of the plate, and formed the second fixed point for the determination of intermediate wave-lengths. In almost all cases the exceedingly bright central-slit image was reversed on account of its great over-exposure, and so formed a fine line upon which as accurate settings could be made as for the other lines. With an arc current of about 9 amperes taken from the 220-volt supply mains, a total exposure of about 5 minutes, made up as before of a number of short exposures, was sufficient.

3. *Results.*

The wave-length measurements are based upon the values given in the previous paper and in particular upon the bright line at 903·7 A. This wave-length is the value given in the previous paper (*loc. cit.*), but, unfortunately, is not one of those which was determined in the second order spectrum. However, a further line (976·7 A) was obtained on some of the negatives, and the value of its wave-length, assuming 903·7 A as standard, is only 0·1 A less than the value in the former work by using the second-order spectrum. The second-order spectrum was too weak for determining the wave-lengths of the lines from their position in that spectrum, but nevertheless it is hoped that the limit of error of the previous measurements was not greatly exceeded.

In working so close to the central image it was assumed that the spectrum was perfectly normal. The extent to which this assumption is justified can be at once determined, for the error† is equal to $bp^3/24m\rho$, where b is the grating constant, p the distance from the central image, m the order of spectrum and ρ the radius of curvature of the grating. In the present

* Millikan, Bower and Sawyer, 'Astroph. Journ.,' vol. 53, pp. 150–160 (1921).

† Kayser's 'Handbuch,' vol. 1, p. 466.

instance this error would be about 0·1A at wave-length 903·7A, so that the expected accuracy would not require a correction to be made for this factor.

The values obtained, together with Millikan's values for the hot spark, are given in Table I.

Table I.

Millikan.		Author.		
λ	I.	λ	I.	$\nu = 1/\lambda \times 10^8$
360·5	0			
372·1	2 Na?	371·5	1	269179
		382·1*	1	261712
		382·7*	1	261301
384·4	4			
386·4	4	386·1	2	259000
		416·2	1	240269
		417·0*	1	239808
419·8	1	420·3*	1	237925
450·9	1	450·9	1	221779
459·7	6	459·5	3	217628
493·7	1			
499·7	4	499·7	1	200120
511·7	1			
517·6	1			
530·3	2			
533·3	2	533·9	1	187301
538·4	7	538·3	3	185770
543·5	2	543·4	1	184026
549·6	2	549·6	2	181951
		558·0	1	179211
560·5	3	560·5	2	178412
		562·4	1	177809
564·7	3	564·8	2	177054
574·5	6	574·3	2	174125
585·7	3	585·5	1	170794
595·1	5	594·9	4	168095
600·2	1 0?	600·3	1	166583
		605·8	1	165071
609·5	1 0?	609·1	1	164177
		617·0	1	162075
		633·7	1	157803
636·3	3	636·2	2	157183
641·8	5	641·8	3	155812
651·5	6	651·3	5	153539
661·5	0			
		680·6	1	146929
		683·5	1	146306
687·3	8	687·1	7	145539
		690·3	1	144865
		700·6	1	142735
		702·6	1	142328
711·0	0	710·7	1	140706
743·6	0	742·7†	1	134644
749·5	0 0?			
		764·1†	1	130873
		765·4†	1	130651

* Observed in second order only.

† Doubtful second-order line.

Table I—(contd.)

Millikan.		Author.		
λ	I.	λ	I.	$\nu = 1/\lambda \times 10^8$.
786·5	1			
799·9	5	799·6	2	125063
806·7	6	806·2	4	124039
810·0	5	809·6	3	123518
		825·0	1	121212
		832·8†	1	120077
		834·0†	1	119904
		840·6†	1	118963
848·4	0	848·5	2	117855
858·5	5	858·2	7	116523
		864·5	1	115674
		866·4	1	115420
884·8	1	884·2	1	113097
904·1	10	903·7	8	110656
		917·3†	2	109016
936·4	1	937·3	1	106689
945·6	4	945·0	5	105820
954·4	0			
960·6	0			
966·6	0			
977·1	12	976·7	8	102386

† Doubtful second-order line.

The intensities given are estimations of the blackness of the image on the plate and are made on the scale 1–10. It will be noticed that they do not agree with those for the same lines which appeared in the former work. This is on account of the increasing failure of the earlier grating for wave-lengths less than about 1000 A.

Apart from the 903·7 line itself, there are only two lines in the arc in this region which have been observed by other workers, viz., 918 and 584, observed by McLennan and Lang.*

4. *Low-voltage experiments.*

It will be noticed on reference to Table I that, with the exception of the extremely faint line at 360·5 A, the arc spectrum produced with a striking voltage of 220 volts proceeds as far as the hot-spark spectrum, in which several thousand volts were applied,† and can be photographed with a quite short exposure. Consequently an effort was made to use an arc with less striking voltage, and if possible to test the quantum relation as applied to the 386 A

* McLennan and Lang, 'Roy. Soc. Proc.,' A, vol. 95, pp. 258–273 (1919).

† Millikan, 'Astroph. Journ.,' vol. 52, pp. 47–64 (1920).

group, which has been identified by Millikan (*loc. cit.*) as the $L\alpha$ lines of carbon.

If the limit of the L series for carbon be assumed to be 360 A, then from the quantum relation

$$Ve = h\nu$$

we obtain V = 35 volts approx. for λ = 360 A.

It should then be possible to excite these lines by the application of a potential difference of this amount.

The electrical connections of the vacuum-arc lamp were re-arranged, so that the arc was struck on a variable shunt from the main current, an ammeter being included in the arc circuit and a voltmeter connected across the arc itself. A series of photographs was taken with a striking potential of 50 volts. With a current of 6½ amperes, an exposure of 8 minutes sufficed to show the 459 A line, while 386 A was obtained with 20 minutes' exposure. The striking potential was now reduced to 30 volts, but exposures of 60 minutes and 75 minutes respectively failed to give a trace of 386 A, although 459 A came out prominently. Longer exposures could not be given on account of the need of renewal of the carbon electrodes. Various exposures were now tried with 40 volts difference of potential at striking, and it was found that 386 A was faintly but distinctly recorded with an exposure of 25 minutes. It may, therefore, be concluded that the applied potential required to excite the L series of carbon lies between 30 and 40 volts, in agreement with the value given by the quantum relation.

It was immediately noticeable from the negatives that a considerable number of lines in the region 386 A to 900 A were suppressed, in addition to 386 A itself, by reducing the voltage from 40 to 30, and consequently the remainder of the carbon spectrum as far as 2,500 A was photographed with the same two voltages to trace this connection throughout the vacuum region. The results are given in Table II.

It was at first thought that the wave-length given in the 30-volt column of Table II would represent the complete arc-spectrum of carbon. The occurrence of the lines 2297, 2509 and 2512 A shows, however, that there is still the likelihood of the presence of spark lines due to first stage ionisation. But it is well known that there are notable differences in the length of spectrum lines when an image of the arc is formed upon the slit small enough to include the ends of the electrodes in the length of the slit itself. No such image is formed in the present case, but the conditions are not greatly dissimilar, since the arc is as close as possible to the slit, the distance being about 4 cms. The length of the three spark lines mentioned does not exceed 1 mm. and corresponds to the greatest

length at which the arc could be momentarily maintained; that is to say, these lines correspond to the only part of the arc in which ionisation would

Table II.

30 volts.	40 volts.
	386·1
459·5	459·5
538·3	538·3
	543·4
	549·6
	560·5
	564·8
	574·3
594·9	594·9
	636·2
641·8	641·8
651·3	651·3
687·1	687·1
806·2	806·2
	809·6
	825·0
	848·5
858·2	858·2
903·7	903·7
945·0	945·0
976·8	976·8
1010·1	1010·1
1036·2	1036·2
1036·8	1036·8
1066·3	1066·3
1175·6	1175·6 *g*
1247·2	1247·2
1261·2	1261·2 *g*
1277·3	1277·3
	1280·3
1323·8	1323·8
1329·6	1329·6 *g*
1335·7	1335·7 *g*
	1431·6
	1463·3
	1481·7
1560·7	1560·7 *g*
1657·0	1657·0 *g*
S 1751·8	1751·8
S 1760·6	1760·6
1930·6	1930·6
S 2297·1	2297·1
2479·1	2479·1
S 2509·5	2509·5
S 2512·4	2512·4

S denotes probable spark line.
g the mean wave-length only of these groups is given.

be expected to occur. Two other lines, 1752 and 1760 A, present the same appearance, and all five lines are of low intensity. The remaining lines in this part of the table have a length of about 3 mms. and are nearly all of greater

intensity than the lines just discussed. It seems probable, therefore, that they form the "arc" spectrum of carbon.

A word may be said concerning the appearance of the arc at these low voltages. With 50 volts the arc was as persistent as at 220 volts, but considerably less bright when the same current was passing. At 40 volts the arc was similar to that at 50 volts but less bright. With 30 volts, however, the arc would not persist, but gave a flash upon touching the carbons together. The light of these flashes was sufficient to photograph, but the continued action of striking the arc resulted in disintegration of the electrodes, although practically no gas was evolved and no intermediate periods of pumping were required. This disintegration also showed a difference from that obtained with 40 volts and upwards. In the latter case both electrodes were worn smooth at the ends and decreased in length until they failed to touch. The gas evolved indicated a certain combination of the carbon with occluded gases, while the most part of the carbon was thrown off as incandescent particles. At 30 volts, however, the carbons presented a pitted appearance at the surfaces of contact, as if pieces had been pulled out of the one electrode by fusing at a point-contact to the other. It was also noticed in at least one instance that the lower electrode actually grew at the expense of the other, a roughly pyramidal point being formed.

Particular attention may be drawn also to the two lines at 806 A and 809 A, which at fairly high voltages have almost the same intensity. Reduction of the voltage to 30 leaves the former of approximately the same intensity as before, relative to the bright lines of the spectrum, while the latter is not, apparently, excited at all.

5. *Conclusion.*

Millikan in his brilliant work with the hot spark (*loc. cit.*) has shown that to obtain results in this region of shortest wave-lengths it is necessary to have gratings ruled with specially light cut, which cannot be judged by their behaviour in visible spectrum. Furthermore he has used very high potentials and vacua, and thus assured the production and registration of radiations of the X-ray type.

The work now described confirms that gratings ruled in this manner permit the registration of these short wave-lengths. It shows, however, that in the case of carbon, X-rays of the L type can be generated in an arc when the applied voltage is of the order of that given by the quantum relation, and without the introduction of any extraneous supply of electrons, such as a

Wehnelt cathode. In addition, it shows that the vacuum attained by a good mechanical oil-pump is sufficient to allow the passage of these radiations through a distance of at least 2 metres.

The wave-lengths now given show differences from Millikan's spark values similar to those recorded in the earlier paper. They are, indeed, based upon a value 903·7 A, which is 0·4 A less than that given by Millikan, but the expected errors of measurement are not adequate to account for the fact that the values for the arc are persistently lower than corresponding ones for the spark. Whether this indicates a shift towards the red by the intense electric fields used by Millikan it will require further work to determine.

6. *Summary.*

The results here recorded may be summarised as follows :—

(1) The spectrum of the carbon arc in vacuum extends as far in the extreme ultra-violet as that of the spark with the exception of a very faint line at 360·5 A, and about 25 lines have been added to the arc spectrum as already recorded.

(2) The L series of carbon can be excited by a potential of between 30 and 40 volts.

(3) Reasons are given for thinking that a number of lines in the carbon spectrum are true "arc" lines.

(4) Providing the grating will give radiation in the short-wave region, the same technique suffices to photograph the spectrum from 1850 A to 370 A.

I have again to thank Messrs. Adam Hilger, Ltd., for the facilities for this work and for permission to publish the results obtained, and would further acknowledge the help of my assistant, Mr. Barnes.

A Method of Measuring the Velocity of Very Rapid Chemical Reactions.

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(Communicated by Prof. J. N. Langley, F.R.S.—Received June 26, 1923.)

CONTENTS.

§ 1.—*General Principles and the Two Essential Conditions.*

In devising methods for determining the velocity of any chemical reaction there are two experimental problems which invariably arise: (1) To arrange that the chemical system under investigation be made initially unstable in a period of time that is negligibly short in comparison with that taken by the chemical reaction. (2) To record from time to time the stages reached by the system (during its passage from the initial unstable state to the final stable condition wherein the several reacting substances are in chemical equilibrium) by means of methods which take a negligibly short time in comparison with that taken by the chemical reaction.

A perusal of the literature shows that previous investigators have, in the main, restricted themselves to the study of slow reactions, such as may require many minutes or even hours to reach completion. In such cases, both requirements which we have mentioned can be easily met. For the production of the initially unstable condition can be achieved without difficulty by merely mixing the several reacting substances together in proportions far removed from those which prevail when equilibrium has been attained. The time required by the mixing operation can be reduced to a few seconds, and can therefore be neglected when dealing with a process which may last many minutes or even hours. The slow reactions possess a further attraction, in that the procedure for estimating the concentrations of the several reactants at different stages during the progress of the reaction need not be a hurried

one. This permits the use of a wide variety of methods, *e.g.*, polarimetry as in the study of the inversion of sucrose, ordinary titration as in the saponification of esters, and separation of one of the constituents as a gas phase as in the decomposition of diazo-acetic ester by water, *i.e.*, $N_2.CHCOOC_2H_5 + H_2O \longrightarrow OHCH_2.COOC_2H_5 + N_2$ (gas phase).

The dynamical study of slow reactions has thrown so much light upon the general mechanism of chemical reactions that the value of a method for measuring the velocity of rapid reactions can hardly be questioned. But in the case of reactions so rapid that equilibrium is reached within a second or less, such methods as those just mentioned break down completely, and it is necessary to search for new modes of attack.

In a previous paper (1) we have described measurements of the rate at which carbon monoxide displaces oxygen from combination with the blood pigment, hæmoglobin. In several of the experiments reported by us, the chemical process was a very rapid one reaching completion within a space of two seconds. The "initial unstable" condition was obtained by use of the fact that the reaction in question is photochemically reversible. Therefore when the system was illuminated by a powerful beam of light, the concentrations of the reactants adjusted themselves to the new values. A subsequent interruption of the beam of light, which could be performed instantaneously, caused the concentration of the reactants to return to their previous "dark" values. We had thus obtained in the case of this very rapid reaction a solution to the first of the two problems, which, as mentioned in the introduction, invariably arises in connection with the velocity measurements of chemical reactions.

Two separate methods were used for ascertaining the time taken by the system to reach various stages during its return to equilibrium. It is of importance to refer to one only of these two methods here. The solution of hæmoglobin under investigation passed through a vertical tube, in which it was exposed to a strong beam of light (which displaced the system from its dark equilibrium) and then flowed down a horizontal tube which was kept in darkness. Directly the solution had left the light tube, the system of reactants began to return to their position of dark equilibrium, and various cross-sections of the dark tube were examined by the reversion spectroscope (2), the readings of which gave the ratio of the respective concentrations of the two hæmoglobin compounds in this system. From this ratio the value of the concentrations of all the constituents at the cross-section under examination could be calculated. By this arrangement the solution was examined

at a certain instant of time after the return to the dark equilibrium had begun, and yet observation by the spectroscope could be continued for as long a time as might be required. It is clear, therefore, that we had also obtained a solution to the second of the two problems which, as mentioned in the introduction, invariably arises in connection with the velocity measurements of chemical reactions. It was also clear that this method of analysis is applicable to a large number of cases so that the second problem may be considered to be solved for other reactions beside the one we had investigated. Thus provided, we could always arrange that the solution, which contained the reacting system to be investigated, should enter the observation tube in an unstable condition (*i.e.*, with the concentrations of the reacting constituents far removed from values which would give chemical equilibrium) then we had only to devise some optical or other physical method of ascertaining the chemical composition of the moving fluid at different cross-sections of the observation tube.

Unfortunately, the solution which we had obtained to the first problem is only applicable to a few cases, because the photo-chemical device for producing an initially unstable condition is not capable of general application. Very few chemical reactions are photo-chemically reversible, and even in such cases it is also desirable to find some alternative method, for, as Dr. Rideal has pointed out to us, it is not legitimate to assume without proof, that the effects of the light upon the system disappear at the instant at which the light beam is interrupted. Instead, we have sought to devise a mechanical process of mixing together two solutions which must be so rapid, and yet so efficient in action, that complete mixture would be obtained before any appreciable degree of chemical action could have taken place. Granted this ideal had been attained, it would be simple to arrive at an initial unstable system by suitable adjustment of the composition and temperature of the two solutions before mixture.

The basic conditions of an apparatus for measuring the velocity of rapid chemical reactions in the liquid phase are therefore :—

(1) In order that problem (1) above should be disposed of, it is necessary that the thorough mixture of the two solutions should be completed in a time short in comparison with that taken by the chemical reaction.

(2) In order that problem (2) above should be disposed of, it is necessary that all parts of the fluid should travel with uniform velocity down the observation tube. There should also, as mentioned above, be a suitable method of measurement, and the concentrations should be those which are found to give the optimum accuracy.

Now the two parts of condition 1 are mutually antagonistic, since for mixing to be perfect it must also be very prolonged. But in spite of this difficulty, an apparatus has been constructed which fulfils both these conditions with a closeness sufficient for all practical purposes to which it has so far been applied, and at the same time it complies with the requirements of condition (2).

§ 2. *A Description of the Apparatus.*

(*a*) *The principle of the method.*—The principle of the method consists in causing the fluids to be mixed to come together at a high velocity within a restricted space. The high velocity of flow was obtained by forcing the fluids through jets under considerable pressure. The streams of fluid having met one another mixed very rapidly and completely, thus fulfilling condition 1 above. They then passed down the observation tube, the diameter of this tube and the rate of flow being suitable for the fulfilment of condition 2 above.

Several types of mixing chamber were tested, *see* fig. 1. (α) Y-shaped, the two jets connecting with the upper limbs the observation tube with the lower (β) like the glass worker's blow pipe jets, (γ) a circular chamber with the jets entering at the side and pointing at one another, (δ) a circular chamber with the jets entering tangentially so that vortex motion should be produced. (ϵ) similar to (γ) or (δ), but with a very high speed electrically driven stirrer

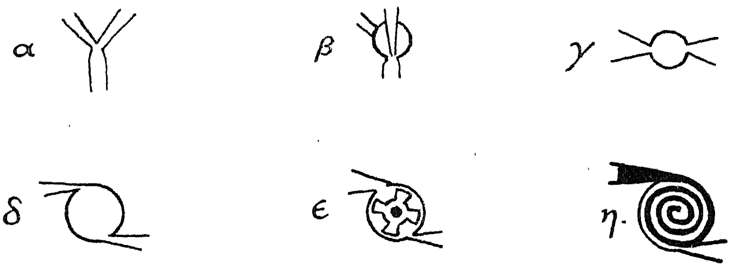

FIG. 1.

inside the mixing chamber. Of these, all except (ϵ) were tested, the first two being found inferior to (γ) and (δ). These latter were given extended tests by methods which will be described in detail in the next section of this paper. It was found that while there was little difference to be found at high pressures, and therefore high rates of flow, at low pressures, and therefore low rates, the tangential type (δ) gave the more perfect mixing as shown in the table below :—

	Type γ Per cent.	Type δ Per cent.
Jet velocity 100 cms. per second	6·0*	1·0*
,, ,, 400 ,, ,, ...	2·0*	1·0*

This superiority of method (δ) is probably due to the vortex motion which is set up. This causes the angular velocity of the fluid near the centre of the chamber (where it passes out into the observation tube) to be greater than it is near the periphery. This difference in angular velocity causes shear to occur between the spiral rings produced by the two liquids, thus producing mixing at their interfaces. (*See* fig. 1, γ.)

The reason for the difference in the efficiency of γ and δ being less at high speeds than at low is probably due to the violence of the eddies set up in type γ at high speeds, which would not occur to the same extent at low ones.

(*b*) *The dimensions of the apparatus*.—The dimensions of two successful types of apparatus are shown in the table below :—

Apparatus number	I	II
Jets, number of	6	4
Jets, diameter in mm.	2·6	2·5
Mixing chamber, diameter in mm.	7·9	12·4
Mixing chamber, depth in mm.	2·6	3·1
Mixing chamber, diameter of outlet in mm.	4·2	6·0
Observation tube, diameter in mm.	6·28	12·8
Observation tube, length in mm.	300	300
Volume of liquid in c.c. passed through apparatus at 600 mm. of Hg pressure	7500	7000
Linear velocity of flow in mm. per second down observation tube at 600 mm. Hg pressure	4000	900
Minimum linear velocity for turbulent flow in mm. per sec.	400	170

The plan of apparatus number (II) is shown in fig. 2 below.

The apparatus enables two fluids to be mixed and observations to be made on the mixed fluid after it has travelled distances ranging from a mean length of 1 cm. to a mean length of 30 cms. from the mixing chamber. Thus supposing the rate of flow down the observation tube to be 100 cms. per second, then the first observation can be made in one-hundredth of a second after the reaction

* These values show the approximate amount of fluid which remains unmixed after passing through the mixing chamber. The method of obtaining these values will be described later.

has commenced, and the reaction can be observed for a total time of one-third of a second. Given a suitable physical method of measuring the concentrations of the constituents at any cross-section of the tube, one can ascertain the stage reached by the reaction after any interval of time between one-hundredth and one-third of a second.

If the linear rate of flow is faster or slower than this, the time between the first possible and last possible reading will be correspondingly altered. Thus the apparatus can be suited to reactions of different velocity by altering the rate of flow.

(*c*) *The method of applying pressure to the fluids.*—The methods available

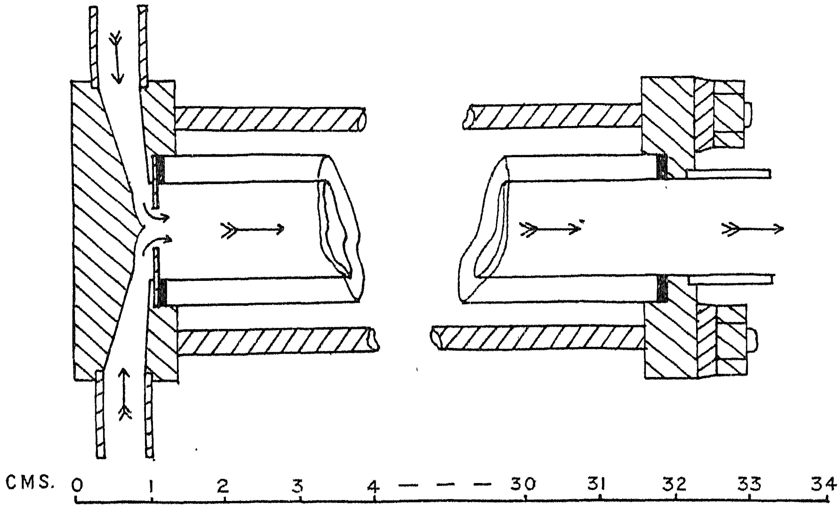

FIG. 2.

would appear to be three in number, (1) hydrostatic head, (2) by a compressed gas, (3) mechanically, *e.g.*, by rotary pumps.

(1) The hydrostatic head is limited in its use to liquids such as aqueous solutions. We have found it very convenient for pressures between 2 cms. and about 2 metres head of fluid. The two fluids under investigation are put into two receptacles and are allowed to flow viâ suitable connections to the apparatus. Since it is the difference in level of the fluids on the entrance and exit side which produces the pressure head, Marriotte's bottles and a constant level overflow should be used wherever possible.

(2) The compressed gas method is applicable to both liquids and gases. In the case of liquids which have been placed in receptacles (*e.g.*, Marriotte's bottles as described), it is only necessary to connect tubes passing through

bungs closing the necks of the bottles to a cylinder of compressed nitrogen or air fitted with an automatic regulator (such as Beards or the universal) and a mercury pressure gauge. We have found this method very satisfactory. When really high pressures are required this also appears to be the simplest method of obtaining them. The containers connecting tubing, etc., should in this case be of suitable design to stand the required pressure with safety.

(3) The mechanical method has advantages where pressures are required which are higher than those which Marriotte's or other bottles will stand since it avoids the cost of supplying special containers. We have used two of the gear wheel type rotary pumps driven by an electric motor with satisfactory results.

(*d*) *The methods of measurement available.*—We have already pointed out in the introduction that in order to measure the velocity of any given chemical reaction the two sets of measurements that are required are (1) the time during which the reaction has been allowed to proceed, (2) the quantitative analysis of the constituents taking part in the reaction at the end of that time. In the apparatus described above the reaction commences immediately the two reagents, entering the mixing chamber by their respective jets, have been brought into intimate contact. The reaction proceeds during the time that the reagents flow down the observation tube. The quantitative analysis at different cross-sections of the observation tube must, therefore, be obtained by methods that are applicable to a moving fluid. Such for example are optical methods involving measurements of (*a*) opacity, (*b*) colour, (*c*) absorption in definite spectral regions, (*d*) mean wave-length or boundary wave-length of absorption bands, (*e*) rotation of plane of polarisation, (*f*) refractive index. But other methods may sometimes be available, such as measurements of temperature, *e.g.*, by thermocouples, or specific inductive capacity or electrical conductivity. The other set of measurements, namely the lengths of time during which the reaction has proceeded, are equal to the intervals which elapse between the instant at which mixture occurs, and the instant at which the fluid reaches the respective cross-sections where determinations had been made. These intervals are readily ascertained from a knowledge of (1) the distance between the cross-sections just mentioned and the mixing-chamber, and of (2) the linear rate of flow. The latter is obviously the quotient of the volume of fluid passing through the apparatus in unit time divided by the area of the cross-section of the observation tube.

§ 3. *Tests of Obedience to Condition I.*

(*a*) *The efficiency of mixing of the fluid leaving the mixing chamber.*—Information on this point was obtained by the following method. Two solutions were prepared :—Solution 1 consisted of N/100 NaOH, to which 0·1 per cent. phenolphthalein was added, and was therefore deeply coloured, whilst Solution 2 consisted of colourless N/100 HCl. These were placed in bottles 1 and 2 respectively, and the bottles connected with the apparatus, a pressure of 400 mm. Hg being applied to the liquids in the usual manner. With both taps full on, a crimson tinted fluid was seen to pass down the observation tube of the apparatus, but on collecting some of the fluid and allowing it to stand the colour was slowly discharged. By keeping the tap from bottle 2 full open, and slowly turning off the alkaline fluid from bottle 1, the pink tint gradually disappeared from the solution until there was only a trace left at the outlet of the mixing chamber. A quantity of the colourless fluid leaving the apparatus was now collected and its P_H,* after thorough mixture, was found by suitable indicators to be 5·6.

The factors which may be responsible for the above phenomenon would appear to be three in number, namely :—

(i) The time taken for chance irregularities in the fluid to disappear by diffusion, convection and stirring.

(ii) The time taken for acid to neutralise base.

(iii) The time taken for the phenolphthalein to tautomerise to the colourless modification which the substance assumes at $P_H < 8$.

We shall postpone the detailed explanation and discussion of the relative importance of these three factors till later in the present section. Our object at the moment is to ascertain the efficiency of the mixing and we shall start with the unfavourable assumption that factors (ii) and (iii) can be neglected, and that factor (i), *i.e.*, imperfect mixing, is entirely responsible for the fact that the final P_H of the thoroughly mixed fluid must be made equal to 5·6 in order that no trace of pink should be visible beyond the outlet of the mixing chamber.

For purposes of calculation it is necessary to make some assumption as to the amount of the coloured variety of phenolphthalein which is seen issuing with the fluid from the orifice of the mixing chamber. The probability is that the amount is small, since the eye will detect quite small amounts of residual colour, because the solution in the rest of the observation tube is

* P_H of x denotes hydrogen ion concentration of 10^{-x} gramme ions per litre.

colourless. The amount is probably well under 1 per cent. Since, however, it is the maximum possible imperfection in mixing that is to be calculated, it is better to assume that the amount is larger than it actually is. The value that we have taken for this purpose therefore is 1 per cent.

Now phenolphthalein commences to turn colour as the P_H is raised beyond about 8, and continues to increase in colour until its full tint is attained at about P_H 9·6. Of the fluid which issues from the mixing chamber, a part will lie on the acid side of P_H 8 and the phenolphthalein associated with it will remain uncoloured, a part also will lie on the alkaline side of P_H 9·6 and the phenolphthalein associated with it will be completely coloured, while the part between P_H 8 and 9·6 will have with it partially coloured phenolphthalein. Now the coloured molecules which we have assumed above to be present to the extent of 1 per cent. are composed of both the two latter. We prefer, however, to make a further unfavourable assumption that they are due entirely to parts of the liquid which exceed P_H 9·6.

With these assumptions we can now proceed to form an estimate of the maximum extent to which the fluid is imperfectly mixed.

It is necessary first to ascertain the hydrogen ion concentration of the fluid obtained by mixing varying proportions of N/100 HCl and N/100 NaOH. This can be obtained by a quite simple calculation, and the results for temperature = 15° C. are given in the following table :—

Table I.

P_H.	Percentage. N/100 HCl	Percentage. N/100 NaOH
4	50·50	49·50
4·4	50·20	49·80
4·8	50·08	49·92
5·2	50·03	49·97
5·6	50·012	49·988
9·2	49·988	50·012
9·6	49·97	50·03

The use of the table may be readily explained as follows :—When 50·012 parts of N/100 HCl are mixed with 49·988 parts of N/100 NaOH, reference to the table shows that a fluid of P_H 5·6 is formed. Thus, in the experiment in which the final mixed fluid was at P_H 5·6, the rate of delivery of bottle 2 must have been 50·012/49·988 times greater than the delivery of bottle 1. According to our assumption, 1 per cent. of the fluid in this experiment had a P_H = 9·6. Now a P_H of 9·6 corresponds, as will be seen from the table, to

a mixture of 49·97 parts of N/100 HCl with 50·03 parts of N/100 NaOH, and if we define portions of the fluid of P_H 5·6 as constituting a mixture of 100 per cent. efficiency, then the degree of mixture of portions of fluid of P_H 9·6 must be equal to $100 \times \frac{49 \cdot 97}{50 \cdot 03} \div \frac{50 \cdot 013}{49 \cdot 988}$ per cent. $= 99 \cdot 8$ per cent. efficiency. Thus 1 per cent. of the fluid just after leaving the mixing chamber will be mixed to the extent of 99·8 per cent. and under, the alkali predominating over the acid, and by symmetry a second 1 per cent. of the fluid will be mixed to the extent of 99·8 per cent. and under, the acid in this portion predominating over the base.

The remaining 98 per cent. of the fluid will be mixed to an extent which exceeds 99·8 per cent. of perfect efficiency. To calculate the average efficiency of mixing for the whole fluid would necessitate a knowledge of the manner in which the 98 per cent. of the fluid is distributed between the efficiencies of 100 per cent. (upper limit) and 99·8 per cent. (lower limit), and the remaining 2 per cent. of the fluid between the efficiencies of 99·8 and 0 per cent. With an assumption which, like the previous ones in this treatment, is almost certainly less favourable than the actual circumstances warrant, the average efficiency of mixture was found to be 99 per cent. Thus there is ½ per cent. unmixed alkali and ½ per cent. unmixed acid.

This value just given is for the fast rate of flow, *i.e.* of 400 cms. per second. With a slow rate of flow, *i.e.* of 100 cms. per second, a slightly less beneficial result was obtained, experiment showed that the final P_H of the mixture of acid and alkali in which only the minimum trace of pink was discernable was 4 (instead of 5·6) for the fast rate, and if this be made the basis of the calculations, the result finally obtained is that the efficiency of mixture is 98 per cent. (*i.e.* 1 per cent. unmixed acid and 1 per cent. unmixed base).

In both cases this approach to perfection would be amply close enough in all cases where the method of measuring the composition of the fluid, as it passes down the observation tube, is only accurate to 2 per cent. or over. Such was the case in the investigation in which we were engaged. Where a more exact method of analysis was available, we should attempt to define between closer limits the composition of the fluid leaving the mixing chamber. The true value for the average efficiency of mixture lies somewhere between 100 per cent. and the figure given above, *i.e.* 99 per cent., the latter being a minimum value on account of the fact that none of the assumptions made use of in obtaining it could possibly have produced too high a value, whereas one at least of the assumptions tended definitely to produce too low a result. For

the purposes of the treatment just given, it was justifiable and indeed desirable to neglect any possible delay which might be caused either by the neutralisation of acid with base or by tautomerisation of the phenolphthalein. We feel, however, that a short discussion of these processes is now desirable. Physical chemists generally assume that ionic reactions, such as the neutralisation of acids by bases, are extremely rapid, and in a later paper we shall advance experimental evidence in favour of this view. The change of colour of indicators is, however, in many cases so slow that it can be measured by the usual methods, for example, in the case of certain indicators Hantzsch found that intervals of half an hour and upwards were required.

In the present instance, information as to the speed of these processes could be readily gained by varying the strength of the acid and alkali employed. Thus in one experiment the one-hundredth normal solutions were replaced by one-tenth normal solutions. If, in the previous test, mixing were really perfect, and the necessity of lowering the P_H of the mixed fluid to 5·6 in order to reduce the pink tint to the merest trace, arose from the slowness of neutralisation and tautomerisation, then it should follow that, in order to secure the same result with N/10 solutions instead of N/100 solutions, the P_H of the final fluid would again have to be 5·6. If, on the other hand, the neutralisation and tautomerisation changes were "infinitely" fast and the mixing imperfect, to the extent indicated by the previous calculations, then it can be shown that with N/10 solutions instead of N/100 solutions the P_H for the minimum trace of pink should be 4·6. If, finally, both mixture and neutralisation and tautomerisation are not quite completed in the mixing chamber, then the P_H required for the minimum trace of pink would lie between 4·6 and 5·6. The actual experiment with the fast rate of flow showed that the P_H required was about 5·6, from which we infer that it is tautomerisation rather than mixture which is not quite perfected in the mixing chamber in the course of these experiments. With the slow rate of flow, on the other hand, similar considerations show that it is mixture rather than tautomerisation which is not quite perfected.

When the taps from both bottles were turned full on, it was found, as mentioned above, that the pink tint of the mixed fluid persisted for some time. The P_H of the final fluid was, however, in this case about 7·4, *i.e.* quite near to the point P_H 8 at which coloured phenolphthalein begins to be formed in appreciable quantities if allowed an infinite time. We believe that the speed of tautomerisation of phenolphthalein is slow when the P_H is nearly equal to 8 but increases very rapidly as the P_H of the solution is reduced below 8, and that when P_H of 5·6 or lower is reached the reaction can proceed extremely

fast. This view can, without much difficulty, be brought into line with Hantzsch's theory of indicators.

(*b*) *The time taken for the mixing of the fluid.*—It is now necessary to ascertain whether the length of time occupied by the mixing process may interfere with the validity of the reaction velocity measurements. In the arguments which follow, it is assumed that the fluid travels with uniform rate of flow down the observation tube. The evidence for this assumption will be found in the next section.

If the fluid as it reached any one cross-section could be divided up into a very large number of parts, and if each part could be separately (and instantaneously) analysed, then a uniform value would only be obtained if the chemical reaction had started at the same instant in all such parts. There are, however, two factors which must certainly prevent this stipulation being realised. These are :—

(i) Some parts of the fluid which enter the mixing-chamber probably become completely mixed (and therefore commence to react) at once, whereas other parts may not become completely mixed until they have almost reached the orifice of the mixing-chamber.

(ii) The fluid which enters the side of the jets further from the observation tube has a longer distance to travel (and therefore a longer time in which to react) than has the fluid which enters at the near side of the jets.

The readings obtained by the measuring instrument at different cross-sections will, therefore, be only average values, and we must now inquire how closely the curve obtained by plotting against time the concentration of the components (as calculated from these average values at different cross-sections of the physical property which is made the basis of measurement) will agree with the true reaction velocity curve.

The extent of heterogeneity possessed by the fluid at any given cross-section is clearly limited by the time interval which separates the earliest and the latest instants, at which the fluid reaching this cross-section could have commenced to react. This time interval cannot exceed that taken by the fluid to travel from the back wall of the mixing-chamber to the orifice, or to travel through a length of the observation tube given by

$$L_0 = \frac{\pi R_m{}^2 L_m{}^2}{\pi R_0{}^2}$$

where R_m is the radius, L_m the length of the mixing chamber and R_0 the

radius of the observation tube. L_0, which may be referred to as "the equivalent length of the mixing chamber," should therefore be made as small as possible. With the small apparatus described above, the value of L_0 was found to be 4·1 mm., and for the wide apparatus 2·9 mm.

Consideration will show that the effect of heterogeneity can be safely neglected if the two extremes values, at every cross-section, of the concentration of the component under investigation differ from one another by an amount less than twice the experimental error of the method of observation. This will be the case, if throughout the whole course of the reaction

$$\frac{L_0}{v} \times \frac{dc}{dt} < \frac{2A}{100},$$

where c is the concentration of the component measured, t is time in seconds, v the linear velocity of the fluid down the observation tube in mms. per second, and A the percentage accuracy of the method of measurement. In order to apply this test, the relation between c and t should be determined experimentally for the reaction under investigation, and by reference to the curve so obtained it can readily be determined whether or not this condition is satisfied. In reactions so swift that the condition cannot be satisfied even when the fastest rates of linear flow are made use of, it is necessary to proceed to more elaborate tests.

These have been based both on experiment and on calculation. The method of experiment consists simply in making determinations of the reaction velocity with different rates of linear flow down the observation tube. With fast rates of flow, the heterogeneity of the fluid reaching different cross-sections must obviously be less than with slower rates of flow. If, however, the results obtained in the two cases agree with one another within the limits of experimental error, then it appears fair to conclude that they must also agree with the results which would be obtained if heterogeneity were entirely absent. As an example, the values shown in fig. 3 may be given.

Both circles and dots were values obtained for the same monomolecular reaction, which will be seen from the figure to be half completed in one-hundredth of a second. But whereas the circles were obtained with a rate of flow of 300 cms. per second and a heterogeneity factor corresponding approximately to that given by the above formula, the dots were obtained with a slower rate of flow of about 100 cms. per second, and a correspondingly higher heterogeneity factor, namely one about three times greater than that given by the above formula. But since the circles and dots plotted in the figure fall with approximately equal accuracy along the same straight line, the velocity measurements

are clearly not affected by the large difference in heterogeneity, or the fact that in the one case it greatly exceeds the value given by the above formula. The conclusion is that in the case of monomolecular reactions the value given by the formula can be safely exceeded by three times. For example at a rate of flow of 300 cms. per second, for which the formula gives one-hundredth of a second, as the time to be occupied by half the reaction a value that could be safely used is one-third of this, namely, one-three-hundredth part of a second. With faster rates of flow correspondingly faster reactions could be studied, and we have recently constructed an apparatus in which a rate of flow of 1000 cms. per second is readily obtainable.

The method of calculation is too complicated to describe in detail, but when applied to monomolecular reactions it agreed with experiment in showing

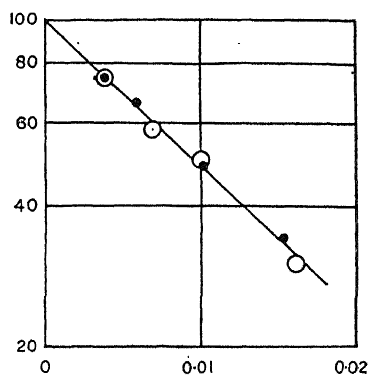

Fig. 3.—Abscissæ. Time in seconds. Ordinates. Logarithm of concentration of component measured. Numerals denote the corresponding values of

$$\frac{\text{actual concentration}}{\text{initial concentration}} \times 100.$$

that heterogeneity was entirely without importance even when the time for half-completion was as short as 1/1000 second, and the value of $L_0\, dc/dt$ ten times greater than $2x/100$. These tests are generally applicable to all classes of rapid reactions. Up to the present, however, we have only had actual occasion to apply them to monomolecular reactions.

A further cause of "heterogeneity" which does not strictly come under condition 1, but which may be conveniently mentioned in this section, arises from the fact that most methods of measurement necessitate the examination of a certain finite width of fluid in the observation tube. Thus, in the case of the spectroscope the width of fluid examined depends on the width of the beam of light which enters the slit of the instrument, and which therefore

contributes to the formation of the parts of the spectrum being used for the measurements. This type of heterogeneity can usually be kept small in comparison with the equivalent length of the mixing chamber by careful attention to detail.

§ 4. *Tests of Obedience to Condition* 2.

(*a*) *The type of flow taking place in the observation tube.*—It is well known that in the stream-line flow which takes place within a smooth cylindrical tube, when the velocity is below that given by Osborne Reynold's formula, the central core of fluid moves with much greater velocity than do the more peripheral parts of the fluid. On the other hand, in the turbulent flow which occurs above the critical velocity there is no such tendency on the part of different parts of the liquid to move with different velocities. The flow of the liquid passing down the observation tube of the apparatus described in this paper is quite different in its appearance to that seen either in streamline flow or in turbulent flow. If, for example, one fluid forced into the mixing chamber was colourless paraffin oil and the other water stained with some water soluble dye, the motion performed in the observation tube was seen to be that of a coarse spiral, the particles of the liquid moving in a direction making an angle of roughly 45 degrees with the long axis of the tube. It is clear that this spinning motion must impose considerable centrifugal force on the fluid, and an important question, therefore, arises as to whether this force is sufficient to draw liquid from the centre core towards the edges. If this were to happen it would tend to increase the velocity of the periphery and decrease that of the central core. In fact in an extreme case the central core might not move at all or might indeed tend to flow in the opposite direction to that taken by the peripheral portion. Additional emphasis was given to this view by the behaviour of small air bubbles which might happen to be in the observation tube. For on admitting the fluids under full pressure into the mixing chamber and then along the observation tube it was seen that the bubbles first left the upper part of the tube and lined up near the central core. They then travelled along in two directions, those nearer the mixing chamber than about 15 cms. moving towards the mixing chamber to take up a fixed position near its outlet, those further away than 15 cms. moving towards the exit tube of the apparatus. If, on the other hand, the fluids were admitted to the apparatus under reduced pressure, all the bubbles tended to be swept out at the exit tube. The important question to be decided was the cause of this movement of the bubbles towards the mixing chamber when the high fluid pressures (and, there-

fore, big centrifugal forces) were obtaining. Was it due to movements of the bubbles only (owing to the difference between their specific gravity and the fluid in which they lay), or was it due to movement of the core of fluid which carried the bubbles along with it ?

Three independent tests were applied in order to answer this question: (1) To cause alternately colourless and coloured fluid to pass down the observation tube, (2) to compare spectroscopic readings taken through the centre of the tube which would therefore include the core with those taken through the periphery of the tube which would not include the core, (3) to compare the spectroscopic readings obtained on one and the same reaction at slow speeds and at fast.

(1) The fluid in bottle 1 was N/100 NaOH containing 0·1 per cent. phenolphthalein, whilst the fluid in bottle 2 was N/100 HCl. With both taps full on a coloured fluid passed down the observation tube, whereas with the tap of bottle 1 turned off slightly the excess of acid caused tautomerisation of the phenolphthalein and thus a colourless mixture resulted. The difference in rate of flow due to the turning off of this tap was trifling, but by doing so the fluid passing down the observation tube could be changed almost instantaneously from coloured to colourless and *vice versa*. By rapidly altering the tap it was possible to cause blocks of colourless and coloured fluid to pass in succession down the observation tube, and any difference in direction or velocity of central and peripheral parts of the fluid would be at once shown. No such effect could be observed however.

(2) The second test was based on the following considerations. In any quickly changing reaction the fluid at any instant will be chemically different from that at a subsequent instant, therefore if there is any return flow near the core of the fluid it will show itself by the readings taken by light that has passed through the core, corresponding to a later stage than those obtained by light that has passed through the periphery. No trace of such an effect has, however, been obtained in any of our experiments.

(3) Lastly, measurements taken at slow rates of flow (at which bubbles do not tend to travel towards the mixing chamber) should differ from those taken at fast rates, if in the latter there is a difference in motion of the core to that of the periphery. No such difference was, however, to be found.

Our conclusion is that all parts of the fluid travel with the same velocity down the observation tube.

(*b*) *The effect of specific gravity.*—The previous experiments show the conditions existing in the observation tube when two fluids of nearly the same

specific gravity are used, but it was possible, however, that different conditions would be met with if the specific gravities of the fluids were very different. It was important to rule out the possibility of such a difference, because in certain of our experiments the salt content of one fluid was very different to that of the other. The matter was tested by placing in bottle 1 a colourless fluid of specific gravity 1·033, and in bottle 2 an aqueous solution of a pigment (specific gravity 1·001) showing marked absorption bands, the strength of which could be accurately ascertained by optical means. The readings obtained on the fast moving fluid both central and peripheral were compared with similar readings made on a stationary intimate mixture of equal parts of 1 and 2. The converse experiment was also tried in which the pigment was added to the solution of greater specific gravity. In neither experiment was any "settling out" of the denser fluid towards the peripheral parts of the observation tube to be detected.

(*c*) *The effect of difference in surface tension.*—As a further test of the mixing powers of the apparatus two fluids were used which show a high interfacial tension. Water was used in bottle 1 and paraffin oil in bottle 2. It was considered evident that if an emulsion of one fluid in the other is obtained at slow rates of flow, this also must be the case at fast, since other experiments show the greater efficiency of mixing obtained with the latter. A slow rate of flow of about 100 cms. per second alone was tried, and it was found that a very fine emulsion of the one fluid in the other was obtained, the water phase being, of course, the continuous one. This experiment shows that a considerable interfacial tension does not prevent a mixture being formed.

(*d*) *The relationship between pressure and rate of flow.*—A knowledge of this relationship is important for two reasons: (*a*) the rate being found at a certain pressure, the rate at other pressures can be obtained without any further measurements, (*b*) from the point of view of design.

Tests performed on the 6-jet apparatus by varying the pressure head on the fluids entering the apparatus and measuring the volume of fluid passed through it per minute, showed that the rate of flow is almost exactly proportional to the square root of the pressure. This is readily seen from fig. 4, which shows rate of flow plotted against the square root of the pressure. An important practical conclusion results from this, namely, that small variations in pressure during an experiment will cause negligible variations in the rate of flow.

(*e*) *The applicability of the apparatus.*—We have already used the apparatus described in this paper for the study of reactions varying in rapidity (*i.e.* time taken for half of the total chemical change to occur) from two seconds

to one-three-hundredth of a second. With longer observation tubes, it would be possible to cope with much slower reactions. On the other hand, there appears to be no reason why, with careful attention to design, the method could not be extended to the measurement of reaction taking one-thousandth of a second or even less. A possible modification, which might be of value in the study of reactions of the highest rapidity, would be to cause the reaction to take place within minute droplets suspended as a spray in a rapidly moving gas phase. The resistance to flow offered by a gas is so very much less than that

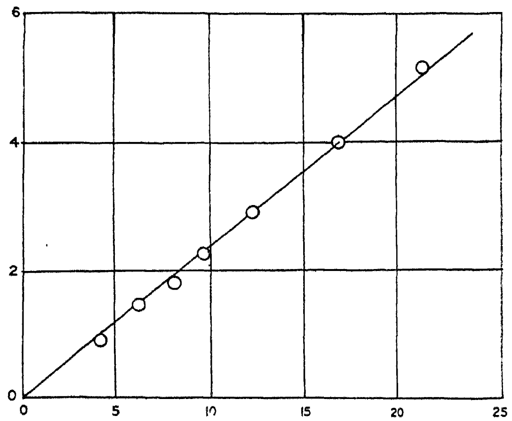

FIG. 4.

offered by a liquid, and therefore much higher linear velocities would be obtainable, and consequently more rapid reactions could be studied. The apparatus might with suitable modifications be also applied to the measurement of rapid reactions between gases.

Our thanks are due to the Medical Research Council for the payment of the costs of this research.

Summary.

In order to determine the velocity of any chemical reaction it is necessary (1) to make the chemical system unstable, (2) to record from time to time the stages reached by the system in its progress towards equilibrium. Both these processes have to be performed so rapidly that the time taken is negligible compared with that taken by the chemical reaction.

The apparatus used by the authors satisfies the above conditions.

By its means two fluids which contain the necessary chemical reagents are caused to mix together at a high velocity within a restricted space. The

mixture then flows with uniform velocity down a glass tube in such a way that estimations of the composition of the fluid can be made at any required cross-section, that is at any required instant of time after mixing.

Of various methods available for forcing the fluids through the apparatus a convenient one is to admit compressed air or gas into the containers which are partially filled by the fluids. Several types of mixing chambers were tested and the greatest efficiency found with one fitted with a number of tangential jets through which the fluids were forced.

The thoroughness of the mixing was tested by using as fluids one-tenth normal soda solution containing phenolphthalein and one-tenth normal acid. The rates of admission were varied until the pink tint of the dye just disappeared. With a knowledge of these rates and with certain assumptions which are fully discussed in this paper, a minimum value for the thoroughness of the mixing can be calculated; with rates of flow down the observation tube of 400 cms. per second not more than 1 per cent. of the fluid remains unmixed. This apparatus has enabled us to measure the velocity of certain chemical reactions. We find that under suitable conditions, the velocities of monomolecular reactions of which the half reaction takes as short a time as one-three-hundredth part of a second can be accurately measured.

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The Kinetics of Hæmoglobin.—II. The Velocity with which Oxygen Dissociates from its Combination with Hæmoglobin.

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(Communicated by Prof. J. N. Langley, F.R.S.)

Contents.

§ 1.—*General Principles of the Reaction.*

The velocity with which oxygen combines with, and is dissociated from, hæmoglobin is a matter of considerable interest both to the physiologist and the physical chemist; to the former because of the all-important part performed by this compound in respiration, and to the latter because hæmoglobin is an almost unique example of a large complex protein molecule which combines with gases, apparently not by adsorption, but in a simple chemical manner defined by the laws of mass action.

There were several preliminary problems which it was necessary for us to solve, before our main experimental investigation could be commenced. Our first major problem was to find some very sudden method of upsetting the chemical equilibrium subsisting between oxygen, hæmoglobin and oxyhæmoglobin in solution. The time taken to upset the equilibrium must be very much shorter than the time taken by the system to regain chemical equilibrium. This problem in the case of the reaction $CO + O_2Hb \rightleftharpoons O_2 + COHb$ was solved by exposing the solution to a powerful beam of light; the latter caused a new position of equilibrium to be taken up, and this could be instantaneously upset by a sudden interruption of the beam of light. The system thereupon returned to its position of dark equilibrium. In order that all parts of the solution shall be passing through the same stages of the resulting reaction it is necessary that the time taken for the equilibrium to be disturbed be of

negligible duration compared with that taken for equilibrium to be regained. Unfortunately, a similar method was not open to us in the present case, for the reaction $O_2 + Hb \rightleftharpoons O_2Hb$ is not appreciably, if at all, affected by a powerful beam of light. The factors upon which the equilibrium of this system depends have been very thoroughly studied by Barcroft and his co-workers in recent years (18); the principal ones are the temperature, the hydrogen ion concentration and salt content of the solution. Calculations showed that even if we had some very sudden method of changing one or more of these factors, the amount by which the system would be displaced would be too small compared with the experimental error of the quantitative methods available. The plan which we have therefore adopted was to prepare a hæmoglobin solution I and another solution II such that if I and II are very rapidly, *but completely*, mixed, the solution immediately after mixing is not in chemical equilibrium, but reaches equilibrium after an interval of time which is long in comparison with the time taken up by the process of mixing. Thus as an example we may mention that, in studying the rate of oxidation of hæmoglobin, solution I consisted of dilute reduced hæmoglobin, whilst solution II consisted of water containing sufficient dissolved O_2 to combine with the hæmoglobin of I. At the instant after the very rapid mixing of I and II the hæmoglobin is still partially reduced, and by methods to be described later the rate at which it subsequently becomes fully oxidised is measured. For this plan to be successful it was necessary to devise a special type of mixing apparatus, the description and testing of which have already been described in one of our previous papers (2).

Our second major problem was to determine the concentrations of the reacting substances at a series of instants after the mixture of the two solutions was completed, and before its reacting substances had reached chemical equilibrium. The first method described in our previous paper (1) was available for this purpose. Solutions I and II flowed into the mixing apparatus and thence down a horizontal tube, which as before could be examined at various different cross sections by means of the reversion spectroscope. In order to determine the concentrations of O_2, reduced Hb, and O_2Hb at different cross sections of the observation tube (and therefore at different instants of time after mixture), it was merely necessary to know the total quantity of O_2 and Hb per c.c. of mixed solution, and to measure the ratio of O_2Hb to reduced Hb at these points. The latter was carried out by a modification of the reversion spectroscope technique, and will be described in full in § 2.

We made preliminary observations both of the rate of oxidation of reduced hæmoglobin and of the rate of reduction of oxyhæmoglobin. For the oxidation experiments, as mentioned above, fluid I consisted of dilute reduced hæmoglobin solution, whereas fluid II consisted of water containing O_2 in solution. For the reduction experiments, however, it was not feasible that solution I should consist of dilute oxyhæmoglobin, and solution II of O_2-free water. For, owing to the shape of the oxygen-dissociation curve of hæmoglobin, no appreciable drop in the percentage of oxyhæmoglobin occurs (except under special circumstances) when 1 part of O_2-free water is mixed with 1 part of oxyhæmoglobin solution of the concentration (*i.e.* 0·2 to 0·4 per cent.) suitable for our experiments. We had, therefore, to seek instead for some chemical reducing agent, which when mixed with an oxyhæmoglobin solution would not react directly with the oxygen, whilst it was still united with hæmoglobin, but would combine with the O_2 in physical solution and would thus cause the oxyhæmoglobin to split off its oxygen in an endeavour to restore the chemical equilibrium between O_2Hb, reduced Hb and physically dissolved oxygen. It was also necessary that the reducing agent should combine with the dissolved oxygen so quickly that no appreciable amount of oxygen, once dissociated from the hæmoglobin, should recombine with the latter again. If a reducing agent with these properties could be found, then it would follow that the observed rate of reduction of oxyhæmoglobin would be solely determined by the rate of the reaction $O_2Hb \longrightarrow O_2$ and Hb, and not be retarded to any appreciable extent by the reverse reaction O_2 and $Hb \longrightarrow O_2Hb$.

Preliminary experiments indicated that the reducing agent sodium hydrosulphite $Na_2S_2O_4$ appeared to fulfil these conditions admirably. The reduction experiments with the aid of this substance offered much smaller practical difficulties than did the oxidation experiments, and the theoretical interpretation of the latter is also rendered more difficult by the fact that here we are perforce dealing with two opposing reactions of hæmoglobin instead of a single unopposed reaction as in the case of the reduction experiments. We therefore decided to defer the study of the oxidation velocities to a later paper and to confine ourselves first of all to the reduction velocities of hæmoglobin. Section 4 of the present Paper therefore gives the evidence on which we assume that $Na_2S_2O_4$ reduces O_2Hb in the manner stated above, whilst the remaining sections are devoted to an investigation and discussion of the factors which influence the rate of reduction of oxyhæmoglobin.

§ 2.—*The Estimation of the Concentrations of Oxy- and Reduced Hæmoglobin in Solution.*

Introduction.—The initial amounts of oxygen, oxyhæmoglobin and reduced hæmoglobin present in the unmixed solutions being known, it is possible to ascertain the subsequent concentrations of these substances in the mixed fluid at any moment, if the relative volumes of the two mixing fluids is known, and if the ratio of the amount of oxy- to reduced hæmoglobin can be determined at any moment. The latter could be obtained by causing the mixture to flow with uniform velocity down the observing tube and by making use of one of the following quantitative methods :—

(*a*) Spectrophotometry, *e.g.*, Hufner's method.

(*b*) Krogh's method of spectroscopic comparison (3) between the absorption bands of the solution in the observation tube with those of oxy- and reduced hæmoglobin solutions placed in the compartments of a double wedge-shaped trough.

(*c*) A colorimetric method depending on a comparison between the colour of the solution in the observation tube and that in a double wedge-shaped trough filled as above, the colour change from vermilion to crimson being increased by viewing the solutions by means of the complementary method of illumination previously described by one of us (4). Thus a suitable piece of signal green glass caused the colour to change from orange through neutral grey to purple.

(*d*) The method which we have actually used, *i.e.* to employ the reversion spectroscope previously described by one of us (5) in the following manner :—

Principle of the Method Adopted.—One compartment of a double-wedge shaped trough is filled with a solution of oxyhæmoglobin, and the other compartment is filled with a solution of the same strength of reduced hæmoglobin. If light that has passed through this trough be analysed by a spectroscope, then it is found that examination of one end of the trough shows the bands of oxyhæmoglobin while the other end shows the bands of reduced hæmoglobin, intermediate positions showing the bands of various mixtures of these substances according to their relative thicknesses.

An additional trough is now filled with a solution of Carbon Monoxide Hæmoglobin, and placed between the double-wedge trough and the light source so that the beam of light first passes through this single trough, then

through the double-wedge trough, and finally through the spectroscope. Let us suppose that the thickness of the single trough multiplied by concentration of COHb contained therein, *i.e.* $(T \times C)$ COHb = maximum thickness of the O_2Hb compartment of the double-wedge trough × concentration of O_2Hb contained therein, *i.e.* $(T_{max.} \times C)O_2Hb$.

An examination of the absorption bands shows that, when the double-wedge trough is shifted as far as possible in one direction (*see* fig. 1 A), the

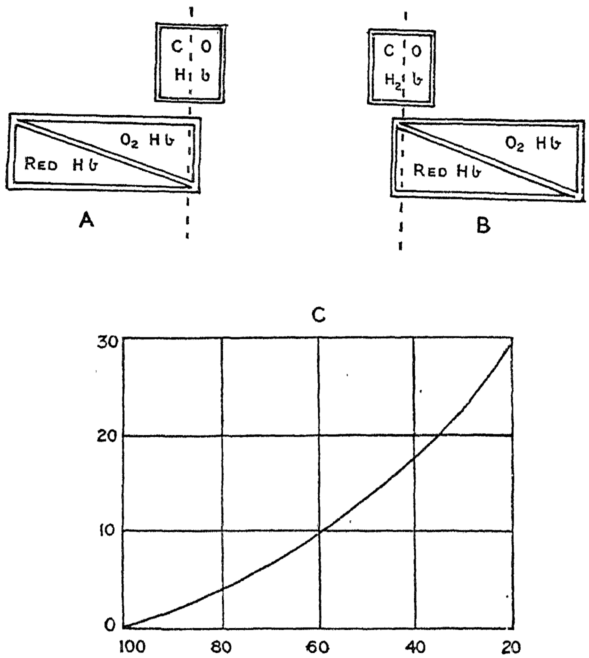

Fig. 1.—A. Shows beam of light passing first through single trough containing COHb, then through maximum thickness of the compartment of the double wedge trough which contains O_2Hb, before finally reaching spectroscope.

B. Shows beam of light passing first through single trough containing COHb, then through maximum thickness of the compartment of double-wedge trough which contains reduced Hb, before finally reaching spectroscope.

C. Calibration Curve—

Abscissæ = Percentage oxyhæmoglobin.

Ordinates = Difference in scale units between spectroscope reading for 100 per cent. O_2Hb and spectroscope reading for x per cent. O_2Hb.

position of the bands in the spectrum is the same as of those of a single hæmoglobin solution in which 50 per cent. of the hæmoglobin is combined with O_2, the remaining 50 per cent. with CO. When, however, the double-wedge trough is shifted as far as possible in the opposite direction (*see* fig. 1 B), the

bands now appear very fuzzy and slightly to the violet side of the bands of a single hæmoglobin solution fully saturated with CO. When the double wedge trough is shifted to an intermediate position, the absorption bands also move to a position intermediate between their two extreme positions in A and B, their exact position in the present instance depending upon the ratio of O_2Hb : reduced Hb traversed by the beam of light. By leaving the COHb trough *in situ*, and by suitable adjustment of the double-wedge trough, we can therefore measure the position of the α band of the spectrum for a series of different values of the ratio $(C \times T)$ O_2Hb to $(C \times T)$ reduced Hb. Having obtained a calibration curve of this kind, we can readily measure the percentage of O_2 hæmoglobin in any single Hb solution in which part of the hæmoglobin is combined with O_2 and the remainder is reduced Hb. The COHb trough is left *in statu quo*, whereas the double-wedge trough is replaced by a vessel of such dimensions that when the unknown Hb solution is placed in this vessel the total concentration of hæmoglobin (oxidised and reduced) in unknown solution $\times$ thickness of vessel $= (C \times T_{max.})$ for O_2Hb (or reduced Hb) in double-wedge trough.

The position of the α band is then determined, and this, with the aid of the calibration curve, gives us the value R of the ratio $\frac{(C \times T) \text{ for } O_2Hb}{(C \times T) \text{ for reduced Hb}}$ of the unknown hæmoglobin solution. But since $T_{O_2Hb} = T_{\text{reduced Hb}} =$ thickness of vessel containing the unknown hæmoglobin solution

$$R = \frac{\text{concentration of } O_2Hb}{\text{concentration of reduced Hb.}}.$$

Experimental Details.—Calibrations, by the above method, were made for four different values of the ratio $\frac{(C \times T)_{COHb}}{(C \times T_{max.})_{O_2Hb}}$; the concentration of the solutions being so adjusted that the absorption bands were in all cases of the optimum breadth and density for spectral examination. The results are shown in Table I. Each figure in the Columns headed I, II, III, IV, V represents the mean value of ten spectroscopic readings.

No readings were taken for values of $\frac{100 \times (C \times T)_{O_2Hb}}{(C \times T_{max.})_{O_2Hb}} < 23 \cdot 0$, for below this limit the absorption bands become so fuzzy and indefinite that accurate measurement is impossible. The results given in Table I are also shown graphically in figure 1c. $\frac{100 \times (C \times T)_{O_2Hb}}{(C \times T_{max.})\ O_2Hb}$ is plotted horizontally, whilst vertically is plotted the difference between the spectroscope reading corre-

Table I.

$\left[\dfrac{(C \times T) \text{ for } O_2Hb}{(C \times \text{maximum } T) \text{ for } O_2Hb} \times 100\right]$.	Spectroscope readings.				
	I	II	III	IV	V
100	106·5	103·8	95·5	99	94·5
88·8	104·5	101·5	93	96·7	92·4
66·8	not observed	97·1	87	91	87·6
56·5	97	93	85·2	not observed	83·7
45·5	91	88·5	80·9	83·6	79·2
34·4	86·2	84	not observed	79·7	75·7
23·6	79·2	76	—	73	not observed

$(C \times T)_{COHb} : (C \times T_{max.})_{O_2Hb} : (C \times T_{max.})_{\text{reduced Hb}}$.

As (I)	35 :	65 :	65.
(II)	43 :	57 :	57.
(III)	50 :	50 :	50.
(IV)	50 :	50 :	50.
(V)	52 :	48 :	48.

sponding to $(C \times T_{max.})_{O_2Hb}$ and that corresponding to $(C \times T)_{O_2Hb}$. The graph shows that within the experimental error the same calibration curve holds good not only for both observers, but also for all values of $\dfrac{(C \times T)_{COHb}}{(C \times T_{max.})_{O_2Hb}}$ between 35/65 and 50/50. This fact simplifies very considerably the determination of the percentage O_2Hb in an unknown solution. The COHb trough is filled with a solution of COHb of such strength that firstly the ratio of

$$\frac{(C \times T)_{COHb}}{C_{\text{Total Hb}} \times \text{thickness of vessel containing unknown solution}}$$

lies between 35/65 and 50/50, and that, secondly, spectral bands formed by light which has passed through the COHb and the unknown solution are of the optimum quality. A set of readings is first taken with the COHb trough and the unknown solution in place. The unknown hæmoglobin solution is removed, saturated with O_2 (by shaking with air), replaced and a second set of readings with the reversion spectroscope is then carried out. The mean of the first set of readings is subtracted from the mean of the second, and reference to the calibration curve gives the abscissa which corresponds to the value of the difference between the two readings as ordinate. The abscissa, so found, is the oxyhæmoglobin percentage of the unknown solution.

Example :—Spectroscope reading for Hb solution containing percentage O_2Hb = X (unknown) was 84·3.

Spectroscope reading for same solution containing 100 per cent. O_2Hb was 94·3.

Difference = 10 units.

Therefore X = Abscissa corresponding to ordinate of 10 units = 57 per cent. O_2Hb.

Accuracy of the Method.—Inspection of the calibration curve (see fig. 1c) shows that the shift of the α band produced by substituting a solution of Hb containing 25 per cent. O_2Hb for one containing 100 per cent. O_2Hb amounts to about 25 units on the spectroscope scale, *i.e.* 1 unit shift on the spectroscope scale corresponds on the average to 3 per cent. change in percentage O_2Hb. The absolute accuracy, however, varies at different parts of the curve. Thus a change ot percentage O_2Hb from—

100 to 90 causes a change in spectroscope reading of about 2 units.
70 to 60 causes a change in spectroscope reading of about 3 units.
40 to 30 causes a change in spectroscope reading of about 5·3 units.

Since previous experience has shown that the reversion spectroscope can usually be relied upon to read to an accuracy of 1 scale unit, it is therefore to be expected that the measurement of percentage O_2Hb will in the range 100–90 be correct to about 5 per cent., in the range 70 to 60 to about 3 per cent., and in the range 40 to 30 to about 2 per cent., etc. (though in the latter range the increasing fuzziness of the bands tends to reduce accuracy).

These facts have to be borne in mind when applying this method of measurement to particular problems. Thus, in the case of the reduction velocity experiments described below, the logarithm of the observed percentage O_2Hb is plotted against time, and therefore measurements in the 90–100 per cent. range are just as valuable as those in the 60 to 70 per cent. range and the 30–40 per cent. range. For an experimental error of 5 per cent. in the 90–100 per cent. range causes an error in the logarithm of the percentage of $\log 95 - \log 90 = \cdot 023$, which differs but little from the error in the logarithm of the percentage caused by an error of 3·5 per cent. in the 70–60 per cent. range, and by an error of 2 per cent. in the 40–30 per cent. range respectively. With $O_2 - Hb$ dissociation curves it is quite different ; it will be shown later that observations above the 70 per cent. range are of very little quantitative value in this connection.

§ 3.—*The Description of a Typical Experiment.*

(*a*) *The Preparation of the Blood Solution.*—Well mixed defibrinated blood, usually from a sheep, was filtered through fine muslin and stored on ice ready for use. Experiments with it were either done the same day, or the blood was borated and the experiments done during the two successive days. A solution of this blood was prepared by adding the requisite quantity to a measured volume of ordinary tap water. When the measuring apparatus with small diameter observation tube (6·28 mm.) was to be used the solution was approximately 1 part blood in 40 parts water, which corresponds very nearly to a molecular concentration of hæmoglobin of $2 \times M/10{,}000$ (if the molecular weight of hæmoglobin is taken to be 16,000).

When the larger apparatus was to be used (12·8 mm. diameter observation tube) a solution of half the above strength (1 in 80) was prepared. A small portion of one of these solutions was now placed into a small test tube made of glass of the same internal diameter as that forming the observation tube of the apparatus to be used.

A solution of 1 part blood in 160 parts water was now prepared, and this having been very thoroughly shaken with thrice renewed coal gas some of the solution was placed in a parallel-sided glass trough 10 mm. wide inside.

The test tube and the trough having been filled as above were placed between the light source and the spectroscope in order to see if the absorption bands have the optimum width for the subsequent measurements.

If this was not found to be the case suitable proportional modifications were made in the dilutions of the two solutions, until by trial and error the correct strength had been found. The bulk of the solution, having been brought to this corrected strength, was poured into bottle I connected to the observation apparatus.

(*b*) *The Preparation of the Solution of the Reducing Agent.*—It was found that a fresh solution of sodium hydrosulphite is acid in reaction, and the solution was therefore neutralised with soda, before being used for a reduction experiment. It was further found that the acidity increased somewhat on shaking with air, so presumably a similar but smaller increase in acidity would occur when the sodium hydrosulphite combines with the oxygen which it robs from hæmoglobin. On this account the solution of the reducing agent was also heavily buffered, in order that but little change in the P_H of the mixed solution could occur during the progress of the reduction.

The volume of standard soda (NaOH) required to bring the reducing agent

itself to various P_H was ascertained by titration, using Methyl Red as indicator from P_H 4·9–6, Brom-Thymol Blue from P_H 6·1 to 7·4, Cresol Red from P_H 7·4 to 8·0, and Thymol Blue from P_H 8·3–9·2.

Table II shows the quantity of soda (20 per cent. solution) necessary to adjust 10 litres of solution (= standard volume prepared) containing 40 gms. $Na_2S_2O_4$ (standard concentration of reducing agent) to different P_H's.

Table II.

P_H	5	5·5	6·0	6·5	7·0	7·5	8·0	8·5	9·0
c.c. soda	5	6·5	10·0	19·0	30·0	42·0	46·0	47·7	48·0

In cases where the total volume of solution or the concentration of the reducing agent differed from the standard values, the amount of soda added was varied in proportion.

The buffered fluids used were for P_H 4–5·6 Clarke's acetic acid-sodium acetate fluid, for P_H 5·6–7·0 Clarke's acid potassium phosphate-sodium hydroxide fluid, for P_H 8–9 an ammonium chloride-ammonia buffered fluid. This was preferred to the boracic acid-sodium borate fluid because of the relative costliness and insolubility of the latter reagents. At certain P_H's where several buffered fluids of different chemical composition were available, experiments were performed to ascertain whether a change in the salts present would change the velocity of the reaction. With these exceptions, the use of the above buffered fluids was adhered to. The mixed solutions of reducing agent, soda and suitably adjusted buffered fluid were poured into bottle II connected to the observation apparatus.

(*c*) *The Preparation of the Observation Apparatus.*—This apparatus was cleaned from time to time in two ways. Firstly, by driving tap water through in the reverse direction to that taken by a fluid under measurement. This process would tend to clear from the jets small foreign bodies which might be partially blocking them. Secondly, by passing 1 per cent. hydrochloric acid through the apparatus which would dissolve insoluble lime salts and other precipitates which had been deposited on the inside of the apparatus by the fluids passed through it. The jets of the apparatus were now connected with bottles I and II by means of wide-bore rubber pressure tubing. If fast rates of flow were to be used, the top connections of the bottles were joined with ordinary pressure tubing to either a compressed air main or a cylinder filled with compressed nitrogen. In either case a suitable mercury manometer, a pressure reduction valve and pressure equaliser were included

in the circuit. The latter consisted of a large closed vessel of 20 litres capacity. The connection of this in the circuit tended to reduce variations of pressure on the surfaces of the fluids in bottles I and II. The air contained in the connections between the bottles and the measuring apparatus and in the latter itself was readily driven out by releasing a slow stream of fluid from both bottles at the same time that the rubber tubes were thoroughly shaken by hand.

If, on the other hand, slow rates of flow were to be used a different method of starting the flow of the fluid had to be adopted, namely, by connecting the exit tube of the apparatus to a water-driven vacuum pump by suitable rubber connections. This caused a temporary rapid flow of liquid through the apparatus which helped to eliminate air bubbles. The exit tube of the apparatus was now rapidly transferred to a narrow cylindrical vessel from which the fluid overflowed into a suitable receptacle. Since the bottles I and II which fed the apparatus stood roughly 60 cms. above the cylindrical vessel above referred to, there was a difference in the level of the liquids connected to the entrance and exit pipes of the apparatus of 80 cms. approximately. The exact difference in level was measured from time to time during an experiment and carefully noted. From these values the rate of flow of liquid through the apparatus could be ascertained, since it had been found by experiment that the rate of flow varies as the square root of the difference of level.

(*d*) *The Measurement of Temperature and Rate of Flow.*—Two other measurements were made during the course of an experiment; one was the temperature of the mixed fluid leaving the apparatus, the other was the quantity of fluid passing through the apparatus in a given time.

With slow rates of flow 1 minute was adopted as standard; with very fast rates the standard was 15 seconds. This test was made in addition to the measurement of the hydrostatic head (and the gas pressure in the bottles when fast rates of flow were in use) in order to be certain that none of the jets was partially obstructed by some chance foreign body.

(*e*) *The Adjustment of the Reversion Spectroscope.*—Having connected the apparatus to the bottles and prepared it for an experiment as described above, the spectroscope was adjusted in position in relationship to the observation tube. It was essential for our purpose that the beam of light illuminating the spectroscope should pass through the horizontal diameter of the tube; this adjustment was effected by placing against the tube a metal plate which just obstructed the light coming through the upper half of it. The spectroscope held in a horizontal position was now raised or lowered on its carriage until on

looking down the eye-piece the lower half of each of the spectra was seen to be illuminated. The spectroscope was then clamped into position and henceforward remained at the same level during all the readings in the experiment, including those required for determining the positions of the bands of the 100 per cent. oxyhæmoglobin solution to be mentioned later. Since the carriage moves along a plane parallel to that of the observation tube, the thicknesses of the two hæmoglobin solutions which were traversed by the beam of light remained constant throughout the experiment, without the necessity of continually repeating the adjustment described above. Between the observation tube and the light source were placed a metal diaphragm perforated with two small apertures and the parallel-sided trough containing the carboxy hæmoglobin solution (usually 1 part whole sheep's blood in 160 parts tap water). The light source, diaphragm and trough were all mounted on the same carriage as the spectroscope so that they could be moved together. The light from the ½-watt "opalite" lamp first passed in turn through the two apertures in the metal diaphragm, then through the 10 mm. layer of COHb solution in the trough, then through the observation tube and finally entered the reversion spectroscope.

The metal diaphragm had three functions: (*a*) it protected the eye of the observer at the spectroscope from stray light from the light source; (*b*) it prevented heating of the trough and observation tube; (*c*) it protected the greater part of the solution in the trough from the action of light which tends to displace carbon monoxide from combination with hæmoglobin and to substitute oxygen instead. In order to avoid still further the effects of rise of temperature or catalytic action of light on the solution in the trough, the latter was thoroughly stirred from time to time during the progress of an experiment.

(*f*) *The taking of the Readings of O_2Hb.*—In order to calculate the percentage of oxyhæmoglobin corresponding to the various spectroscopic readings taken at different cross-sections of the observation tube during an experiment, it was necessary, for reasons explained in Section 12, to ascertain the spectroscopic reading corresponding to 100 per cent. O_2Hb. For this purpose we required to introduce into the observation tube a solution of the same total hæmoglobin concentration as that used in the experiment, and further provide that all the hæmoglobin in this solution should be combined with oxygen. Such a solution was simply prepared by diluting some of the blood solution drawn from bottle I with an equal volume of water. (The Hb concentration was identical with the Hb concentration of the mixed fluid

during an experiment, since the rates of the delivery of bottles I and II were found to be identical.) The solution was then placed in a vessel, into which the end of the exhaust tube of the apparatus was introduced. By disconnecting the tube connected with bottle II and connecting it instead with the water-driven vacuum apparatus, some of the diluted oxyhæmoglobin solution was sucked into the observation tube. When the latter had been washed through several times a screw clip was placed on the exhaust tube, leaving the observation tube filled with O_2Hb solution and ready for the taking of the readings. During these readings the trough containing the carbon monoxide hæmoglobin was left in position just as during an experiment.

§ 4.—*The Reduction of Oxyhæmoglobin by Sodium Hydrosulphite—Evidence as to the Nature of the Mechanism.*

In our reduction experiments, as we have already mentioned, dilute solutions of O_2Hb and of sodium hydrosulphite were made up in separate bottles I and II respectively. From these they were driven into the mixing chamber, and thence down the observation tube of the measuring apparatus as described in the previous section. Observations of different cross-sections of the latter were then made by means of the reversion spectroscope. At cross-sections very near the mixing chamber end, the hæmoglobin was found to be completely oxidised; but as the spectroscope was moved away from the mixing chamber the hæmoglobin was found to be more and more reduced, until eventually a cross-section was reached, where the hæmoglobin appeared to be completely reduced and no trace of oxyhæmoglobin could be detected (provided, of course, the concentration of $Na_2S_2O_4$ in solution II was sufficient to combine with all the oxygen in solution II). Determinations of the percentage O_2Hb at different cross-sections between this "end-point" and the mixing chamber enabled us to measure the percentage O_2Hb at a series of instants, the intervals between which could be readily obtained from the rate of linear flow of the solution down the tube, and the positions of the cross-sections examined. We were thus able to measure the rate of reduction of O_2Hb by $Na_2S_2O_4$. But our object was to determine the true velocity constants of the reaction $O_2Hb \rightleftharpoons O_2 + Hb$, and in order to find out whether either or both of these could be deduced from the observed rates of reduction of O_2Hb by $Na_2S_2O_4$, it was necessary for us first to inquire into the mechanism of the action of $Na_2S_2O_4$ upon O_2Hb.

It has been known for a considerable time that sodium hydrosulphite combines with dissolved oxygen, and, indeed, Schutzenberger's method (6)

of estimating the quantity of O_2 in physical solution depends upon this fact. Removal of oxygen from physical solution would cause some of the oxyhæmoglobin to dissociate into reduced hæmoglobin and oxygen (the latter passing into physical solution) in an endeavour to restore the chemical equilibrium between the three substances. We therefore felt bound to conclude that the reduction of O_2Hb by $Na_2S_2O_4$ is, at any rate in part, brought about by the following coupled reaction :—

(*a*) $O_2Hb \rightleftharpoons Hb + O_2$ (in physical solution)

O_2 (in physical solution) $+ Na_2S_2O_4 \longrightarrow$ oxidation products of $Na_2S_2O_4$.

But it is possible that this mode of reduction may be accompanied and perhaps overshadowed by either :—

(*b*) A direct reaction between $Na_2S_2O_4$ and O_2Hb, *i.e.* $Na_2S_2O_4 + O_2Hb \rightleftharpoons Hb +$ oxidation products of $Na_2S_2O_4$. Thus Haldane (7) has advanced evidence that there was direct chemical action between methæmoglobin and ammonium sulphide, and presumably, therefore, a similar combination between methæmoglobin and sodium hydrosulphite exists. This suggests that a similar reaction may occur in the case of hæmoglobin and sodium hydrosulphide. Or we may find :—

(*c*) A formation and subsequent decomposition of an intermediate compound between $Na_2S_2O_4$ and O_2Hb, *i.e.*

$Na_2S_2O_4 + O_2Hb \rightleftharpoons Na_2S_2O_4, O_2Hb$.

$Na_2S_2O_4, O_2Hb \longrightarrow Hb +$ oxidation products of $Na_2S_2O_4$.

Thus compounds of this nature are formed between sodium hydrosulphite and organic compounds, specially those containing amido groups (8). Or, lastly, there might be :—

(*d*) A combination of (*b*) and (*c*).

It was necessary for us to find some decisive method of discriminating between these possibilities, and it seemed to us that a promising line of attack would be furnished by a study of the effect of widely varying concentrations of sodium hydrosulphite upon the velocity with which oxyhæmoglobin is reduced.

Fig. 2 shows the result of an experiment in which five different concentrations of $Na_2S_2O_4$, ranging from 0·25 to 4·0 grms. per litre, were employed. In each case the final P_H of the mixed fluid was about 7·4. It will be noticed that all the curves in the figure consist of two well-defined portions :—

(i) A horizontal part or "period of induction," during which no appreciable reduction of O_2Hb takes place. The length of this

period of induction is considerable when the concentration of $Na_2S_2O_4$ is small (*i.e.* about 1 second for concentration = 0·25 grms. per litre), but diminishes rapidly as the concentration of $Na_2S_2O_4$ is increased, until finally when the concentration of $Na_2S_2O_4 = 2 \cdot 0$ grms. per litre the period of induction has practically disappeared.

(ii) A descending part during which the reduction of O_2Hb is very rapid.

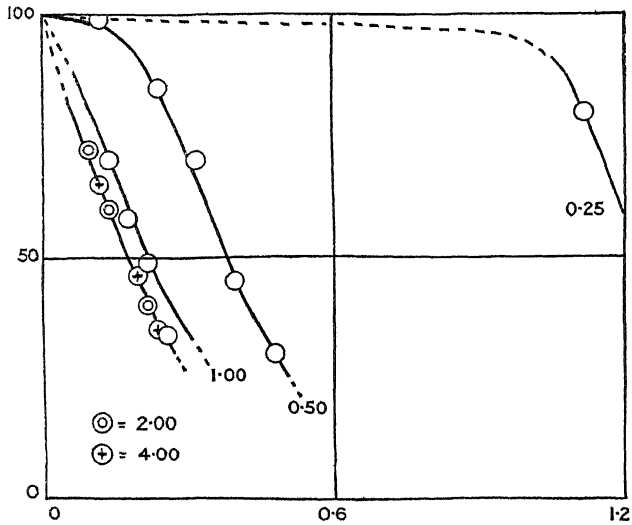

Fig. 2.—Abscissæ = Time in seconds.
Ordinates = Percentage oxyhæmoglobin.
Numerals attached to each curve denote concentration of sodium hydrosulphite in grammes per litre.
Temperature = 11° C.

These parts of the curves for concentrations of reducing agent of 0·5 grms. per litre and upwards are parallel and in the cases of 2 and 4 grms. per litre the values coincide within the limits of experimental error.

These striking results did not take us altogether by surprise, for a previous consideration of the oxygen dissociation curve of hæmoglobin had led us to anticipate that if mechanism (*a*) were the sole mode of reduction, then the curves would very probably be of this character.

The upper of the two curves shown in fig. 3 is the oxygen dissociation curve of the same hæmoglobin solution as that used in the reduction velocity experiments, *i.e.* the volume of O_2 (c.c. at N.T.P.) chemically combined with the hæmoglobin in 1 c.c. of solution when the latter had been equilibrated with gas mixtures containing various known tensions of O_2. The lower curve

gives the volume of O_2 in physical solution at different tensions of O_2. Thus the total quantity of O_2 in 1 c.c. of solution at any oxygen tension X is readily

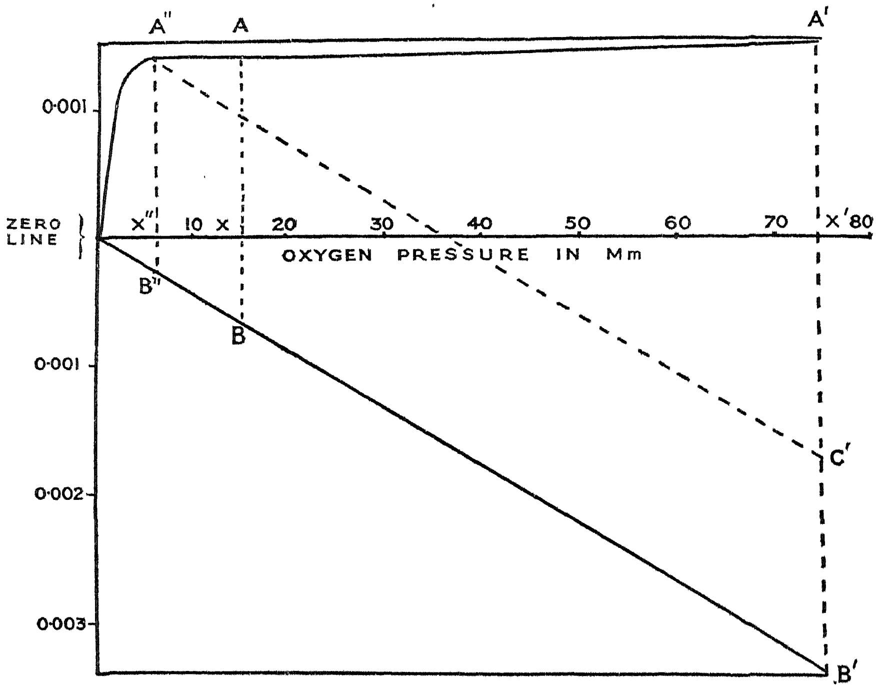

Fig. 3.—Abscissæ = Oxygen pressure in mm. of mercury.

Ordinates (i) above pressure axis = c.c. of oxygen combined with hæmoglobin per c.c. of solution;

(ii) below pressure axis = c.c. of oxygen in physical solution per c.c. of solution.

obtained by drawing through X a line parallel to the Y axis. Let this cut the upper curve at A and the lower curve at B.

Then AX = vol. O_2 per c.c. solution combined with Hb.

BX = vol. O_2 per c.c. solution in physical solution.

AB = Total vol. O_2 per c.c. solution.

Returning now to the reduction velocity experiments, it is clear that, since the O_2 tension in fluid I is zero, and the O_2 tension in fluid II equals approximately the O_2 pressure in the atmosphere which equals 150 mm., the O_2 tension in the resultant solution at the instant after mixing is just complete will be equal to X′, where $X' = \frac{0 + 150}{2} = 75$ mm. The total quantity of O_2 in solution per c.c. at this instant will therefore be given by A′B′. Inspection of the dissociation curve shows that if mechanism (*a*) is the correct one, no

appreciable reduction in the percentage O_2Hb can occur until the oxygen tension in the mixed solution has fallen to X″, where X″ = about 6 mm., *i.e.* until the total volume of O_2 per c.c. has fallen to A″ B″. Draw a line through A″ parallel to OBB′. Let this line cut A′B′ at C′. Then, if mechanism (*a*) is correct, we should expect that first of all a volume of O_2 = A′C′ must be removed out of physical solution by the $Na_2S_2O_4$, and not until this is completed can any appreciable reduction of the O_2Hb begin to take place.

This leads us to a very simple interpretation of the two well-defined portions of the reduction velocity curves.

(i) The horizontal part is due to the time taken by the reaction $O_2 + Na_2S_2O_4$ (period of induction) to proceed far enough to reduce the O_2 in physical solution from a tension of 75 mm. to a tension of roughly 6 mm. The period of induction, therefore, depends solely upon the velocity of the reaction $O_2 + Na_2S_2O_4 \longrightarrow$, and therefore diminishes rapidly as the concentration of $Na_2S_2O_4$ is increased.

(ii) The descending part, on the other hand, depends almost entirely upon the velocity of the reaction $O_2Hb \longrightarrow O_2 + Hb$. For the rate of reduction of O_2Hb (as noted above) is the same for all concentrations of $Na_2S_2O_4$ equal to and greater than 0·5 grm. per litre when once the period of induction has been passed. This we take to mean that in all these cases the concentration of the reducing agent is so great that the O_2 dissociated off from the O_2Hb is removed almost instantaneously, and, in consequence, the velocity of the opposing reaction $O_2 + Hb \longrightarrow O_2Hb$ is negligible in comparison with the velocity of the direct reaction $O_2Hb \longrightarrow O_2 + Hb$. We therefore suggest that the velocity of reduction of O_2Hb in the descending part of the curve is a measure of the velocity of the reaction $O_2Hb \longrightarrow O_2 + Hb$ unopposed and uncomplicated by the reverse reaction $O_2 + Hb \longrightarrow O_2Hb$.

It should be possible, if this theory is correct, to alter the length of the period of induction, but not the rate of reduction, by varying the quantity of dissolved oxygen present in Solution I before mixture. This deduction was readily put to the test by means of three experiments, in which the composition of solution I was as follows :—(i) 95 per cent. O_2Hb, P_{O_2} = 7 mm. approximately (obtained by diluting 1 part of whole oxygenated blood with 40 parts O_2-free water); (ii) 100 per cent. O_2Hb, P_{O_2} = 150 mm. approximately [1 part whole oxygenated blood with 40 parts tap-water]; (iii) 100 per cent.

O_2Hb, $P_{O_2} = 450$ mm. approximately. [1 part whole oxygenated blood + 40 parts oxygenated water.]

The solution II, however, was in each case the same, and contained 2·0 grms. $Na_2S_2O_4$ per litre dissolved in a phosphate buffer mixture of $P_H = 7 \cdot 7$. The results, which are shown graphically in fig. 4, confirmed our anticipations.

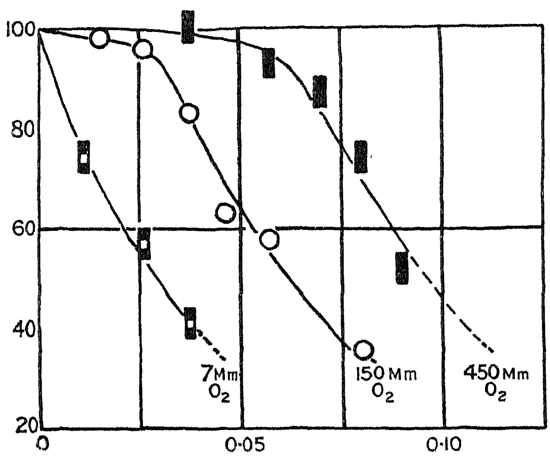

Fig. 4.—Abscissæ = Time in seconds.
Ordinates = Percentage oxyhæmoglobin.
Observations obtained when oxygen pressure in solution was initially
(i) 7 mm. Hg represented by striped rectangles.
(ii) 150 mm. Hg ,, circles.
(iii) 450 mm. Hg ,, black rectangles.
Temperature = 15·5° C.

Curve (i) shows no period of induction, whereas curves (ii) and (iii) show definite periods, the length of that of (iii) being about double the length of (ii). The descending portions of all three curves are parallel, however, within the limits of experimental error.

The results shown in figs. 2 and 4 seem to indicate clearly that neither mechanism (*b*) [direct action between $Na_2S_2O_4$ and O_2Hb] nor mechanism (*c*) [formation and decomposition of an intermediate compound] is playing any appreciable part in the reduction of oxyhæmoglobin. If mechanism (*b*) were operating, it should follow that increase of concentration of $Na_2S_2O_4$ should always cause an increase in the velocity of the reaction, and the curves of fig. 2 should therefore descend more and more steeply, instead of remaining parallel at concentrations of $Na_2S_2O_4$ greater than 0·5 grms. per litre. The fact that an eight-fold increase in the concentrations of sodium hydrosulphite has no detectable influence on the rate of reduction of O_2Hb (after the

induction period has been passed) appears quite incompatible with the view that sodium hydrosulphite can react directly with oxyhæmoglobin in a manner similar to that in which it may be able to react directly with methæmoglobin.

The difficulties in the way of accepting mechanism (*c*) are no less serious. It might be possible, on this view, to explain why increase of $Na_2S_2O_4$ concentration only raises the reaction velocity up to a certain limiting value. If the formation of the intermediate compound, *i.e.* $Na_2S_2O_4 + O_2Hb \rightarrow Na_2S_2O_4, O_2Hb$ were very fast in comparison with the decomposition reaction $Na_2S_2O_4, O_2Hb \rightarrow Hb +$ etc., then the concentration of the intermediate compound at any one instant of time would be practically constant for all concentrations of $Na_2S_2O_4$ greater than a certain small value, and therefore the rate of formation of reduced hæmoglobin by means of the reaction $Na_2S_2O_4, O_2Hb \rightarrow$ etc., would also be constant. But there is no reason why the latter reaction should not begin immediately after mixture of solutions I and II has taken place. Formation of reduced hæmoglobin should therefore take place by mechanism (*c*) during the period of induction, and by mechanisms (*c*) and (*a*) jointly after the "induction period" is finished. Yet a reference to the third point in curve marked 7 mm. O_2 of fig. 4, and to the first point on curve marked 450 mm. O_2 of fig. 4, shows that no detectable amount of reduced Hb is formed by mechanism (*c*) alone during an interval of time in which no less than 60 per cent. of reduced Hb is formed by mechanisms (*a*) and (*c*) together. This can only mean that mechanism (*c*) is either not operating at all, or that its reactions are progressing at a speed which is negligible in comparison with those of mechanism (*a*). The same conclusion is derived from a comparison of the first point on the curve marked 0·5, with the first point on the curve marked 4·0 in fig. 2. The final, and possibly most searching test, which we have applied to our theory, has been to bring about the reduction of oxyhæmoglobin by a method which did not require the presence of a "foreign substance" to combine with the dissolved oxygen, and to see how closely the results "checked up" with those obtained by the chemical reduction method previously employed. We found that if

Solution I contained blood diluted 1 in 80 with water previously freed from O_2,

Solution II contained O_2-free water strongly buffered with an acetate mixture to P_H 5·6.

Then the fluid, at the instant after mixture, had percentage $O_2Hb = 95$, $P_H = 5·6$, and the final mixture after the reaction was complete had percentage $O_2Hb =$ about 50, $P_H = 5·6$.

These two solutions were driven by compressed nitrogen through the small apparatus, at a high velocity. Measurements of the percentage O_2Hb at various instants were made in the usual manner, and the values obtained were plotted as black rectangles in fig. 5.

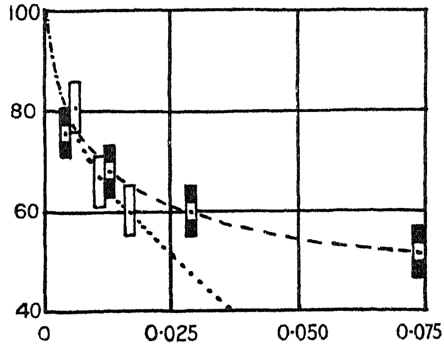

FIG. 5.—Abscissæ = time in seconds.
Ordinates = percentage oxyhæmoglobin.

In the second experiment, 4·0 grms. per litre of $Na_2S_2O_4$ was added to solution II, whilst solution I remained of the same composition as above, and the P_H of the final mixture was again = 5·6. The values obtained are shown by white rectangles in fig. 5. The agreement at early stages of the reaction will be seen to be good. This is not the case at later stages, but this disagreement is to be expected, as we will now proceed to show.

. The conditions in the former experiment are not identical with those which we suppose to obtain in the latter; for in the former experiment neither of the products of the reaction are removed, and as the reaction progresses the back action will necessarily become more and more prominent. But without making any particular assumptions in regard to the chemical kinetics of the back action $O_2 + Hb \longrightarrow O_2Hb$, we can show that the time taken by the system to perform the first half of its journey (*i.e.*, to proceed from 100 per cent. O_2Hb to 75 per cent. O_2Hb) should be the same, or, at most, only one-third as long again as the time taken to proceed from 100 per cent. O_2Hb to 75 per cent. O_2Hb when there is no back action. On any theory of the action of $Na_2S_2O_4$ other than that which we have put forward, there should not necessarily be any connection between the "auto reduction" curve and the chemical reduction curve; but on our theory the "auto-reduction" curve and the chemical reduction curve should lie very close to one another during the first part of their course. Our observations leave no doubt that this is indeed the case, even though the special conditions of the

auto-reduction experiment increased the experimental error of the determinations two-fold.

This concludes the evidence which we offer as to the mechanism by which sodium hydrosulphite reduces oxyhæmoglobin. We have been at pains to make it as complete as possible, on account of the great advantages which the chemical method is found to possess when compared with the auto-reduction method. The latter is only about half as accurate as the former, and, further, can only be employed under extremely limited conditions. But by use of sodium hydrosulphite we have been able to study the effect of wide variations in important factors such as P_H, temperature and hæmoglobin concentration, upon the reduction velocity constant. In addition, the solutions require no elaborate preparation, but can easily be made up in the space of a few minutes.

§ 5.—*Quantitative Interpretation of Results and Effect of* P_H *upon the Velocity of Reduction.*

Our next problem is to find a quantitative explanation of the results previously given, and also of those to be described in the remainder of the paper. It is natural to turn to the Law of Mass Action for a velocity equation to express the rate of reduction of oxyhæmoglobin; but for this purpose it is necessary that we should know the exact chemical equation or equations by which the reversible reaction between oxygen and hæmoglobin is to be represented. At the present time, however, this question is still under dispute. Hüfner's original conception was that the reaction would be expressed by means of the equation:

$$1 \text{ mol Hæmoglobin (Hb)} + 1 \text{ mol } O_2 \rightleftharpoons 1 \text{ mol } O_2\text{Hb} \quad \ldots\ldots\ldots\ldots (1)$$

The researches of Bohr (9) showed, however, that the equilibrium relation deduced from this equation did not accord with experimental observations; and the dissociation (or better equilibrium) curves obtained by Barcroft and his associates agree very closely with quantitative deductions drawn from the theory first proposed by A. V. Hill (10), namely, that:—

1 mol Hb_n combines with n mols of O_2 to form 1 mol $(\text{HbO}_2)_n$.

In a series of recent papers Hill (11, 12 and 13) has, by use of his theory, succeeded in explaining quantitatively a large number of the phenomena exhibited by hæmoglobin in concentrated solution. The rate of reduction of oxyhæmoglobin should on Hüfner's theory be given by the equation:

$$\frac{d\,(O_2\text{Hb})}{dt} = -k\,(O_2\text{Hb}) + k'\,(O_2)\,(\text{Hb}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

but on Hill's theory by

$$\frac{d\,([O_2Hb]_n)}{dt} = -k\,([O_2Hb]_n) + k'\,(O_2)_n\,(Hb_n) \ldots\ldots\ldots\ldots\ldots \quad (4)$$

When, however, the reduction of O_2Hb is brought about by $Na_2S_2O_4$ the oxygen in physical solution is removed so quickly that its concentration, *i.e.* (O_2) in the above equation, is inappreciable; therefore the second term on the right hand side of both velocity equations can be neglected and the two above equations then reduce to precisely the same form, viz. :—

The equation $\frac{d\,(O_2Hb)}{dt} = -k\,(O_2Hb)$ and $\frac{d\,(O_2Hb)_n}{dt} = -k\,(O_2Hb_n)$. Both these, when integrated between instants of time t_1 and t_2, give $\log_e (O_2Hb)$ at $t_1 - \log_e (O_2Hb)$ at $t_2 = k\,(t_2 - t_1)$, *i.e.*, $\log (O_2Hb)$ when plotted against t should give a linear relationship.

This has been tested in the case of the results shown in figs. 2 and 4 of the previous section. As before, t is plotted horizontally, whilst vertically the percentage of oxyhæmoglobin is replaced by the logarithm of the oxyhæmoglobin percentage. The points were found to fall well within experimental error upon a straight line. Fig. 6 shows one example.

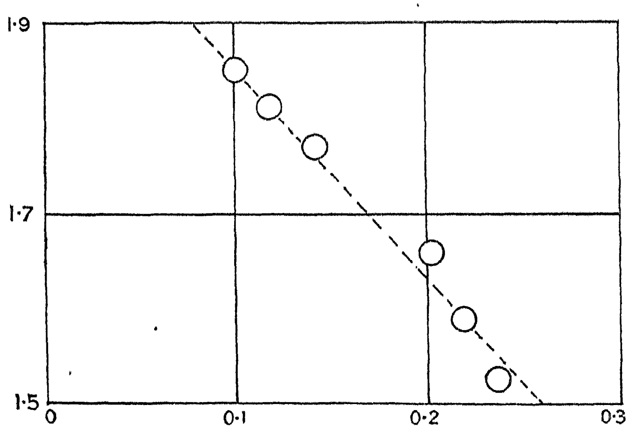

FIG. 6.—Abscissæ = time in seconds.
Ordinates = log of percentage of oxyhæmoglobin.

In spite of the good agreement between calculated and experimental results, it is not clear without further consideration that the use of a single velocity equation can be justified. Hæmoglobin is now generally believed to be an amphoteric electrolyte, dissociating principally as an acid on one side of the iso-electric point ($P_H = 6 \cdot 6$ according to Michaelis) and as a base on the other side of the iso-electric point. A solution of oxyhæmoglobin

cannot, therefore, be expected to be homogeneous, but will contain oxyhæmoglobin both in ionised and unionised form. L. J. Henderson (14) suggested that ionised and unionised hæmoglobin had quite different affinities for oxygen, and this assumption has become a very important part of Hill's theory of hæmoglobin combinations (11, 12 and 13). It may therefore be anticipated that ionised and unionised hæmoglobin will not possess the same reduction velocity constant, and since oxyhæmoglobin is present in both these forms in solution we ought really to use two, or perhaps more, velocity equations. A study of the effect of P_H upon the observed reduction velocity was expected to throw light on this question, for an alteration in the P_H of the solution ought to cause an alteration in the distribution of O_2Hb between the ionised and unionised forms.

In these experiments bottle I contained a solution of oxyhæmoglobin obtained by diluting whole blood with tap water to an appropriate extent for spectroscopic measurement (usually about 1 part blood to 40 parts water). The P_H of this solution was in all cases $= 7 \cdot 4$ approximately. Bottle II contained a buffer solution of P_H varying from $5 \cdot 6$ to 11, and, in addition, 4 grms. of $Na_2S_2O_4$ per litre + sufficient NaOH to bring the $Na_2S_2O_4$ to the same P_H as the buffer. The strength and composition of the buffer solutions were prepared from the directions of Clark (15) and their P_H determined by means of the usual indicators; the P_H of the final mixed solution which passed through the apparatus was assumed to be the same as the P_H of the original heavily buffered solution in bottle II.

The results shown in fig. 7 are highly instructive. The rate of reduction is slowest in alkaline solution ($P_H 10$) and does not rise appreciably as the hydrogen ion concentration is lowered until $P_H\ 7 \cdot 7$ is reached; between $P_H\ 7 \cdot 7$ and $P_H\ 6 \cdot 3$ there is a sudden rise. Below $P_H\ 6 \cdot 3$ there is a further but probably more gradual increase in the reduction velocity; but owing to several experimental difficulties, *e.g.* the high speed of the reaction and the tendency of the acid solution to decompose the hæmoglobin with formation of hæmatin, and to decompose the sodium hydrosulphite with precipitation of sulphur, we have not as yet studied the reduction velocity at P_H's below $6 \cdot 3$ with the same thoroughness as at P_H's above $6 \cdot 3$.

The length of the period of induction was also found to vary with P_H in a manner which could in part be explained by the effect of P_H upon the dissociation curve of oxyhæmoglobin. The other factors of importance in this connection did not appear to lie within the scope of the present inquiry because they were obviously connected not with the reduction of the

hæmoglobin, but with the effect of P_H on the rate of oxidation of the reducing agent. The rate of reduction is in this experiment eight times and on the

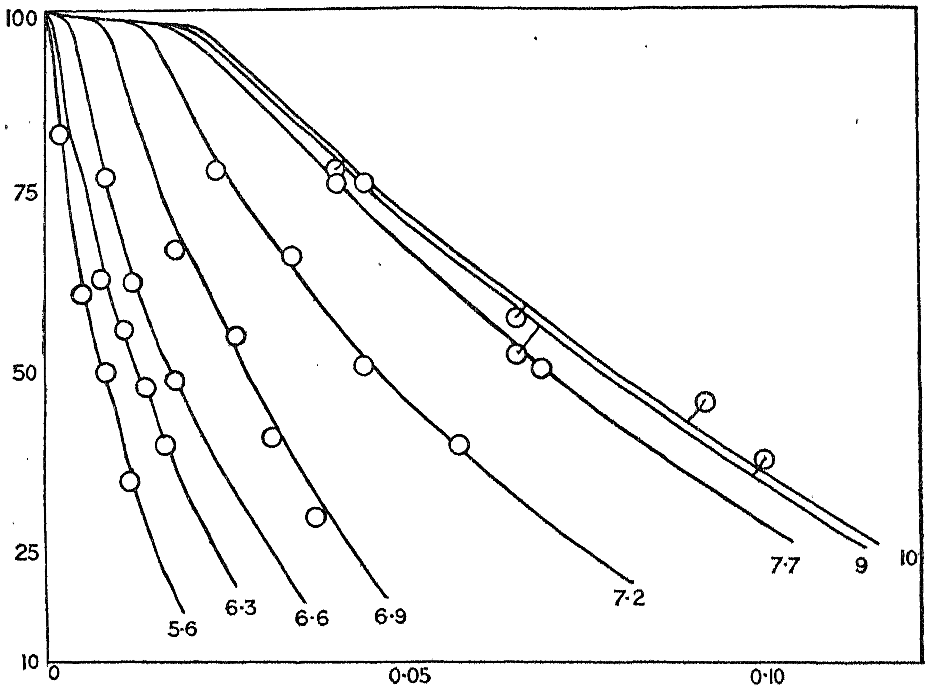

Fig. 7.—Abscissæ = Time in seconds.
Ordinates = Percentage oxyhæmoglobin.
Numerals attached to each curve indicate P_H of solution.
Temperature 15° C.

average from six to seven times slower at $P_H = 7 \cdot 7$ and over than at $P_H = 6$ and under; but the P_H effect is in no way due to any change in the mode of action of the sodium hydrosulphite, for in control experiments we showed that a threefold increase in concentration of $Na_2S_2O_4$ did not alter the observed reduction velocity either at $P_H = 5 \cdot 6$ or at $P_H = 9$. We can only conclude that ionised and unionised oxyhæmoglobin yield up their combined oxygen at quite different rates.

When the oxyhæmoglobin percentages of fig. 7 are replaced by their logarithms and the latter plotted against time, a number of straight lines are obtained for all P_H's investigated. These are shown in fig. 8.

The validity of the logarithmic relationship was further tested by varying the concentrations of oxyhæmoglobin. Two pairs of experiments were carried out, the first pair at P_H 5·6 with blood of 1 in 40 in the narrow apparatus and

with blood of 1 in 80 in the wide apparatus, the second pair at $P_H = 9$ with blood of 1 in 40 and 1 in 80 in their respective apparatus. According to the

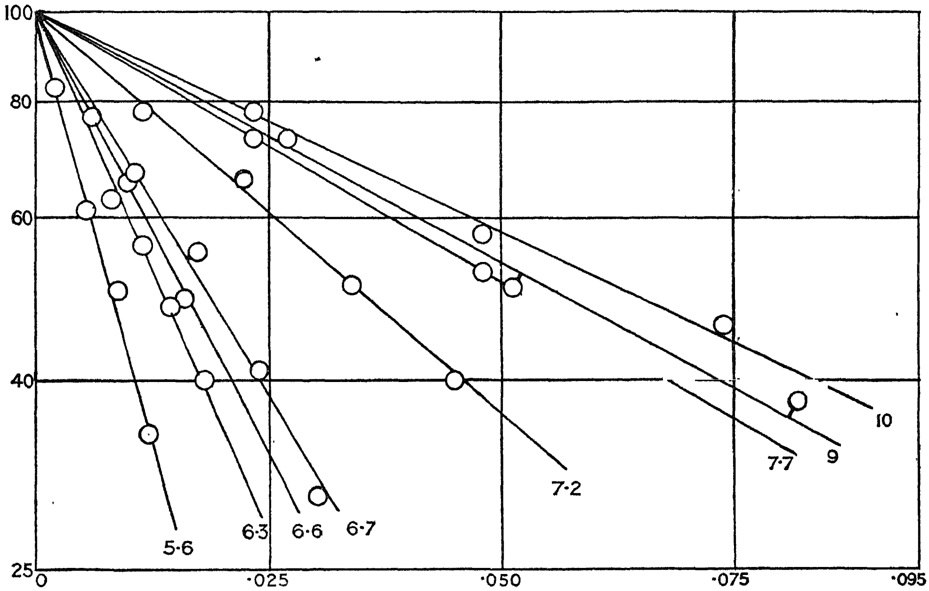

Fig. 8.—Abscissæ = Time in seconds.
Ordinates = logarithm of oxyhæmoglobin percentage; numerals on left of ordinate axis indicate corresponding value of oxyhæmoglobin percentage.

velocity equation which we have put forward the proportionate change in concentration of oxyhæmoglobin in a given time should be independent of the absolute concentration of oxyhæmoglobin. Thus log O_2Hb plotted against t should give the same straight lines at $P_H = 5 \cdot 6$ for blood 1 in 40 as for blood 1 in 80, and similarly for $P_H = 9$. The experiments confirmed this conclusion. The value of the reduction velocity constant for each P_H was calculated from the values plotted in fig. 8 in the following manner. Each point, obtained in an experiment at a given P_H, was surrounded by a rectangle, the dimensions of which indicated the size of the experimental error incurred in the determination. The angle with the X axis made by the steepest straight line, which would just pass through these rectangles, was measured; so also was the angle made by the flattest possible line. The arithmetic mean of the tangents of these two angles was assumed to represent the value of the reduction velocity constant k at the P_H in question. The possible error in the value of k was rather large, actually amounting to $\pm$ 20 per cent. The results are plotted in fig. 9 which shows the relation between k, so calculated, and P_H.

The curve is rather similar in appearance to an ionisation curve of a

monovalent weak acid, with an ionisation constant of about 2×10^{-7}. We believe that this resemblance, together with the considerations now to be developed, supply a quite simple interpretation of the P_H effect.

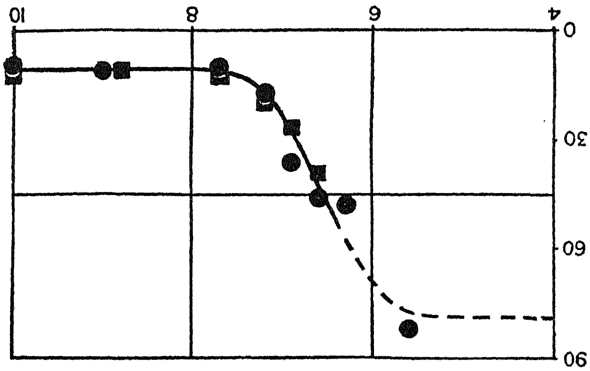

FIG. 9.—Abscissæ = P_H of solution.
Ordinates = Value of reduction velocity constant.
Squares represent results obtained in experiment on one sample of blood.
Circles ,, ,, ,, ,, another sample of blood.

Theoretically the hæmoglobin molecule is capable of releasing a large number of hydrogen and hydroxyl ions, and indeed the recent work of van Slyke and his associates (16) shows that at $P_H = 7 \cdot 4$ the single molecule can dissociate at least five hydrogen ions. It is, however, well known that in the case of polyvalent acids of simple chemical constitution, the loss of one hydrogen ion impedes the loss of a second, and the loss of the second impedes the loss of the third and so on. Thus the ionisation constant for the first dissociation of phosphoric acid H_3PO_4 is equal to 1×10^{-2}, for the second $8 \cdot 8 \times 10^{-8}$ and for the third $3 \cdot 6 \times 10^{-13}$. It therefore seems likely that in the case of the protein molecule, which is formed by the union of a large number of feebly ionisable amino-acids, the loss of a hydrogen ion from one amino-acid group will tend to inhibit the loss of a second hydrogen ion from any other amino-acid group in the immediate neighbourhood.

We are inclined to believe that the five (or more) dissociated hydrogen ions are split off from parts of the hæmoglobin molecule which are widely separated from one another. If *one* hydrogen ion is liberated from the hæmatin portion of the molecule, *i.e.* from a position close to the peculiar grouping which holds the dissociable oxygen molecule, then it would seem unlikely that a second hydrogen ion should be dissociated from any grouping in the immediate neighbourhood. On similar grounds it also seems unlikely that the loss of a hydrogen (or hydroxyl) ion from a position in the molecule distant

from the hæmatin portion will appreciably affect the velocity with which oxygen combines with or dissociates from the hæmoglobin, since presumably the point of attachment and of release lies within the hæmatin portion. On the other hand, the release of the single hydrogen ion from the hæmatin will be certainly expected to have an effect upon the velocities of oxidation and reduction. In this assumption we are adhering closely to the view of Brown and Hill (13).

Let λ_a = proportion of hæmoglobin which has lost the single hydrogen ion from the hæmatin portion,

and let λ_u = proportion of hæmoglobin which has not lost the single hydrogen ion from the hæmatin portion,

i.e. $\lambda_u + \lambda_a = 1$,

also let k_a and k_u = the corresponding reduction velocity constants. Then it should follow that the resultant velocity constant $k = k_a \lambda_a + k_u \lambda_u$; and therefore that $dy/dt = (k_a \lambda_a + k_u \lambda_u) y$, where y is the total concentration of oxyhæmoglobin present provided that the interionic changes of oxyhæmoglobin are very much more rapid than the reduction velocities.

The manner in which this equation is derived is not difficult to explain. Let us suppose for the sake of argument that k_u is greater than k_a. Then after an infinitesimally short interval of time dt the concentration of unionised oxyhæmoglobin would be lowered by the reduction process to $\lambda_a y - k_u \lambda_u y\, dt$, and the concentration of ionised oxyhæmoglobin to $\lambda_a y - k_a \lambda_a y\, dt$. Since k_u and k_a are different, the concentration of unionised oxyhæmoglobin would be now too low to allow the ratio $\dfrac{\text{concentration of unionised oxyhæmoglobin}}{\text{concentration of ionised oxyhæmoglobin}}$ to remain equal to $\dfrac{\lambda_u}{\lambda_a}$ which is the equilibrium relation necessitated by the P_H of the solution being kept constant. An ionic reaction between the unionised oxyhæmoglobin and the ionised oxyhæmoglobin must therefore take place simultaneously during the interval dt, and if this ionic process is very much more rapid than the reduction process then the $\dfrac{\text{concentration of unionised hæmoglobin}}{\text{concentration of ionised hæmoglobin}}$ will in reality emerge at the end of the interval still very closely equal to $\dfrac{\lambda_u}{\lambda_a}$, nor will the ionic processes, if of relatively great rapidity, allow the ratio to be appreciably displaced from the value at the end of any subsequent finite interval. This consideration,

however, does not invalidate the proposition that the total fall in hæmoglobin concentration, *ie* — dy, during the interval dt is given by

$$- dy = (k_u \lambda_u + k_a \lambda_a)\, y\, dt$$

or

$$- dy/dt = (k_u \lambda_u + k_a \lambda_a)\, y,$$

and this equation must remain true throughout the course of the reaction provided that the $\dfrac{\text{concentration of unionised oxyhæmoglobin}}{\text{concentration of ionised oxyhæmoglobin}}$ remains constantly equal to $\dfrac{\lambda_u}{\lambda_a}$.

The following hydrostatic arrangement provides a useful and very complete analogy. Two bottles A and U with cross-sections equal to λ_a and λ_u respectively, where $\lambda_a + \lambda_u = 1$ are connected together by a wide tube at their base. Each bottle is also provided with a capillary tube through which it can discharge the water contained within it. The resistance of the capillary supplying A is equal to $k_a \lambda_a$, *i.e.* the volume of water driven through the capillary per second by a water head of h cms. is equal to $k_a \lambda_a h$. The resistance of the capillary supplying U is, in the same units, equal to $k_u \lambda_u$. The two capillaries can be opened or closed at will. The water in the two bottles is initially at the same level y. When the two capillaries are opened, the volumes of the water flowing through them will not be proportional to the cross-sectional areas of the bottles A and U, unless k_a and k_u are equal. But any difference in level which might arise in this manner through k_u not being equal to k_a will be eliminated at once by passage of water through the wide connecting tube, which owing to the relatively slight resistance presented by a tube of wide bore can take place far more rapidly than the outflow through the capillaries. Thus the levels of water in the bottles A and U will fall at the same rate, and, further, the $\dfrac{\text{volume of water in U}}{\text{volume of water in A}}$ will remain equal to $\dfrac{\lambda_u}{\lambda_a}$.

Finally, the total volume of water lost by the system in time dt will be given by

$$dV = (k_a \lambda_a + k_u \lambda_u)\, y\, dt,$$

but V (total volume) $= (\lambda_a + \lambda_u)\, y$.
Therefore $dV = (\lambda_a + \lambda_u)\, dy = dy$, since $\lambda_a + \lambda_u = 1$ by definition.
Therefore $dy = (k_a \lambda_a + k_u \lambda_u)\, y\, dt$.

We therefore arrive at a precisely similar equation for the rate of loss of water by this hydrostatic analogue, as for the rate of loss of oxyhæmoglobin in the previous treatment. If the ionisation constant for the dissociation of the hydrogen ion from the hæmatin portion is equal to 2×10^{-7} approximately (from other considerations Hill has calculated that the value is about 5×10^{-7}), then at P_H below $6 \cdot 0$ $\lambda_u = 1$ very nearly, and $\lambda_a = 0$; whereas at P_H's above $7 \cdot 7$ $\lambda_a = 1$ very nearly and $\lambda_u = 0$. Therefore k_u should be given by the constant value of k at low P_H's, and k_a by the constant value of k at high P_H's. λ_a, λ_u at P_H's intermediate between $6 \cdot 3$ and $7 \cdot 7$ can be obtained from the ionisation equation given by a weak acid with ionisation

constant equal to 2×10^{-7}. The values of k within the same range can be calculated from the equation $k = k_a \lambda_a + k_u \lambda_u$ by insertion of the values of λ_a and λ_u just mentioned, together with those of k_a and k_u, which were assumed to be 10 and 70 respectively.* The latter values for k_u and k_a together with an ionisation constant $= 2 \times 10^{-7}$ were found to give the closest agreement between observed and calculated results.

The observed values and the calculated values of k are compared in Table III.

Table III.

P_H	5·6	6·3	6·6	6·9	7·2	7·7	9·0	10·0
Observed value of k	82·0	48·0	46·0	36·6	20·0	10·4	11·7	9·7
Calculated value of k	66·0	52·0	42·0	32·0	23·0	14·0	10·2	10·0

The agreement is moderately good, and the discrepancies could be readily accounted for by the possible errors in the determination of the observed values of k.

It is possible, though so far as we know there is at present no positive evidence, that the hæmatin portion may also dissociate a hydroxyl ion which likewise influences the rates of oxidation and reduction of hæmoglobin. In that case, the simple equation $k = k_a \lambda_a + k_u \lambda_u$ would have to be replaced by one containing three terms on the right-hand side, *i.e.*, $k = k_a \lambda_a + k_b \lambda_b + k_u \lambda_u$. In the still more general case in which there are "n" different forms of oxyhæmoglobin which oxidise and reduce at different rates, we should write $k = k_a \lambda_a + k_b \lambda_b + k_n \lambda_n + k_u \lambda_u = \Sigma k\lambda + k_u\lambda_u$ provided, as stated above, that the inter-ionic changes are far more rapid than the reduction velocities. Even in so general a case we should still be justified in employing a single velocity equation, but the interpretation of the P_H effect would be more complicated than the one which we have put forward.

The assumption that the inter-ionic changes are extremely rapid plays such a fundamental part in our theoretical interpretations, that we have been most anxious to find means of deciding whether or not this hypothesis is justifiable. It is true that physical chemists generally assume that all ionic reactions take place instantaneously, but no previous experimental work, with which we are acquainted, gives us a definite warrant for assuming that the

* Whilst this paper was in the press, Dr. Widmark kindly drew our attention to an exactly similar equation put forward by himself in 1920, to account for the effect of P_H upon the velocity constant of the reaction

$$CH_3COCH_2COOH \longrightarrow CH_3COCH_3 + CO_2.$$

ionisations take place in less than a hundredth part of a second. In our experiments the time taken by the ionic changes can only be neglected if it is considerably shorter than a thousandth part of a second. The importance of settling the question was further urged upon us by the fact that in all the experiments mentioned so far the oxyhæmoglobin solution started from bottle I at $P_H = 7 \cdot 4$, and therefore very much more extensive changes in ionisation of the oxyhæmoglobin must have occurred when the P_H of the final mixture was $5 \cdot 6$, than when it was $7 \cdot 7$. Part of the difference between the observed values of k at $P_H = 5 \cdot 6$ and $7 \cdot 7$ respectively might be due to this fact, unless the ionic changes were in reality extremely rapid.

Fortunately we have been able to test the matter by means of two very simple pairs of experiments. In the first pair of experiments the composition of the fluids was as follows :—

	Fluid I.	Fluid II.	Mixed fluid.
(*a*)	25 c.c. blood $3 \cdot 4$ gms. KH_2PO_4 $0 \cdot 22$ gms. NaOH per litre	4 gms. $Na_2S_2O_4$ $3 \cdot 4$ gms. KH_2PO_4 $0 \cdot 49$ gms. NaOH per litre	$12 \cdot 5$ c.c. blood $3 \cdot 4$ gms. KH_2PO_4 $0 \cdot 355$ gms. NaOH 2 gms. $Na_2S_2O_4$ per litre
	$P_H = 6 \cdot 3$	$P_H = 6 \cdot 3$	$P_H = 6 \cdot 3$
(*b*)	25 c.c. blood $1 \cdot 36$ gms. KH_2PO_4 $0 \cdot 38$ gms. NaOH per litre	4 gms. $Na_2S_2O_4$ $5 \cdot 44$ gms. KH_2PO_4 $0 \cdot 33$ gms. NaOH per litre	$12 \cdot 5$ c.c. blood $3 \cdot 4$ gms. KH_2PO_4 $0 \cdot 355$ gms. NaOH 2 gms. $Na_2S_2O_4$ per litre
	$P_H = 7 \cdot 7$	$P_H = 6$	$P_H = 6 \cdot 3$

Inspection of the third column will show that the composition of the mixed fluid was, in the two cases, identical not only in regard to its P_H but in every other respect also. In (*a*) there was no change in the P_H when the two fluids mixed ; therefore there was no change in the ionisation of the phosphate buffer or of the oxyhæmoglobin. But in (*b*), in which the P_H of the mixed solution lay between the P_H's respectively of the separate solution before mixture, considerable alterations in the ionisation both of the inorganic buffers and of the oxyhæmoglobin must have taken place on (and perhaps after) mixing. If such processes were not far more rapid than the reduction of oxyhæmoglobin, we should expect to find differences in the rate of reduction in the two cases. Conversely if (*a*) and (*b*) were to yield the same rate of reduction, then we should feel justified in concluding that the ionic changes both of the buffers and of the oxyhæmoglobin are "infinitely" rapid in comparison with the reduction velocity. Actually our measurements showed that the two rates were, within the limits of our experimental error, identical.

In the sec ond pair of experiments we had—

	Fluid I.	Fluid II.	Mixed fluid.
(*a*)	25 c.c blood 3·4 gms. KH_2PO_4 0·95 gms. NaOH per litre	4 gms. $Na_2S_2O_4$ 3·4 gms. KH_2PO_4 1·83 gms. NaOH per litre	12·5 c.c. blood 3·4 gms. KH_2PO_4 1·39 gms. NaOH 2 gms. $Na_2S_2O_4$ per litre
	$P_H = 7 \cdot 7$	$P_H - 7 \cdot 7$	$P_H = 7 \cdot 7$.
(*b*)	25 c.c. blood 3·4 gms. KH_2PO_4 0·08 gms. NaOH per litre	4 gms. $Na_2S_2O_4$ 3·4 gms. KH_2PO_4 2·70 gms. NaOH per litre	12·5 c.c. blood 3·4 gms. KH_2PO_4 1·39 gms. NaOH 2 gms. $Na_2S_2O_4$ per litre
	$P_H = 5 \cdot 8$	P_H about 11	$P_H = 7 \cdot 7$

Again, the rates of reduction came out identical within the limits of experimental error, which shows that the ionic changes in the oxyhæmoglobin and the phosphate buffer caused by the alteration in P_H from 5·8 to 7·7 also take place more rapidly than do the reduction processes.

This conclusion is of importance, in that it provides a justification for assuming a single velocity equation both in the case of the present reaction and also in the case of the reaction which we have previously investigated (I). At the time when our earlier paper was written we believed that the use of a single velocity equation was only justifiable if the hæmoglobin was either completely ionised or completely unionised. The present treatment shows that the original hypothesis was quite justifiable without the introduction of any such restriction as that just mentioned.

The ionic reactions which we have been discussing are by no means unlike those which bring about neutralisation of acids within the living body. Hitherto there has been no evidence as to the speed with which these neutralisation processes can take place. It seems possible that an extension of the methods described in this paper may eventually yield interesting information upon this subject.

§ 6.—*The Effect of Temperature and Salts.*

I. *Temperature.*—The study of the effect of varying the temperature presented very little difficulty. In the case of temperatures above 13° C. (Lab. temperature), the solution in bottle I, which contained the oxyhæmoglobin, was kept at Lab. temperature, in order to avoid the possible deleterious effects of increased temperature upon the oxyhæmoglobin, whereas the solution in bottle II was warmed up to an extent, which depended upon the final temperature required for the mixed fluid which travelled down the observation tube. For temperatures below 13° C. one or both of the solutions was cooled by ice. Fortunately it was quite unnecessary to employ any thermostats to regulate

the temperature of the reacting fluids. No appreciable change in the temperature of the mixed fluid occurs as it passes from one end of the observations tube to the other. Observations of the temperature of the mixed fluid were made at the beginning and end of each experiment, and in no case was a difference greater than one-tenth of a degree noticed. This close approach to constancy was presumably due to the slowness with which the large volume of fluid lost heat through the poorly conducting walls of the earthenware bottle wherein it was stored, and was thus amply sufficient for our purpose in spite of the high temperature coefficient which the reaction was found to possess. The temperature coefficient of the velocity constant was measured both at $P_H = 5 \cdot 6$ [at which $k = k_u$ according to the previous section] and at $P_H = 9 \cdot 0$ [at which $k = k_a$]. The reaction in the case of $P_H = 5 \cdot 6$ proceeded too fast for the present experimental methods at temperatures above 14° C., but in the case of $P_H = 9$ it was found possible to get measurements at a temperature as high as 28° C. A three-fold increase in the concentration of the sodium hydrosulphite at the highest and lowest temperatures investigated in both cases caused no difference in the observed rate of reduction. We therefore concluded the action of the $Na_2S_2O_4$ remained unaltered throughout the range of temperatures which we employed. The results for the two velocity constants are shown in fig. 10A.

Both have a very high temperature coefficient, *i.e.* about 3·8 per 10° C. for the range investigated.

It follows from Arrhenius' equation for the effect of temperature upon the velocity constant of a chemical reaction (17), that log k when plotted against the reciprocal of the absolute temperature should give a straight line relationship. In fig. 10B the values of log k at $P_H = 5 \cdot 6$ and $P_H = 9 \cdot 0$ respectively have been plotted against the reciprocal of the absolute temperature In both cases the points fall very closely upon a straight line.

Extrapolation of either of these straight lines to a temperature of 37° C. shows that k at body temperature may be expected to be about fifteen times greater than at 14° C. At $P_H = 7 \cdot 4$ a reduction from 100 per cent. O_2Hb to 50 per cent. took about 0·04 secs. at 4° C.; therefore the same degree of reduction should take about 0·0025 secs. at 37° C. This time is negligible in comparison with the time (about 1 second), which the blood corpuscle is generally supposed to spend in passing through a blood capillary in the living organism. If the rate of reduction for the highly concentrated solution of hæmoglobin present in the corpuscle is of the same order as that of hæmoglobin in dilute solutions, then it can be readily seen that, in the case of the sheep

and presumably in other mammals, the rate at which the oxygen can be dissociated from combination with hæmoglobin plays no appreciable part in determining the rate of uptake of oxygen by the tissues.

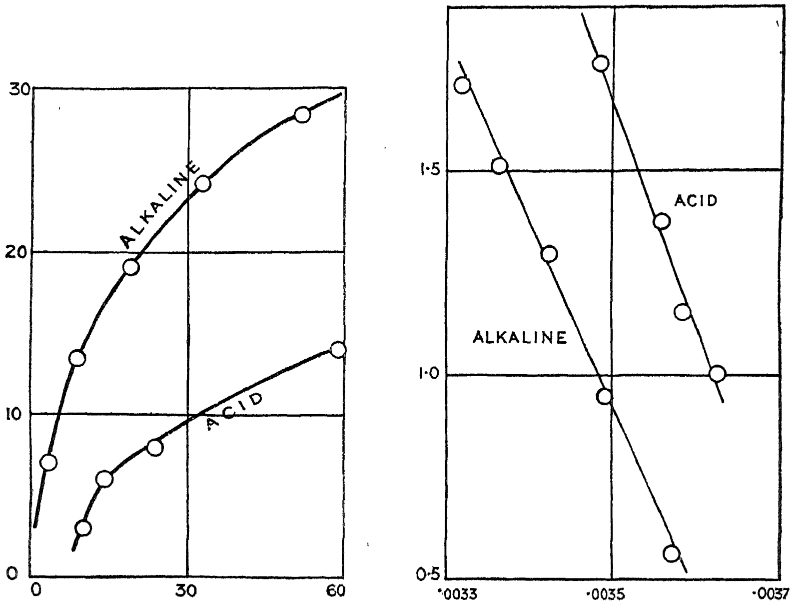

Fig. 10A. Fig. 10B.

Fig. 10.—A. Abscissæ = Value of reduction velocity constant.
Ordinates = Temperature in degrees Centigrade.
B. Abscissæ = Reciprocal of absolute temperature.
Ordinates = Logarithm of reduction velocity constant.

II. *The Effect of Salts.*—Barcroft and his co-workers (18) have shown that the addition of salts to concentrated solutions of dialysed hæmoglobin produced a marked shift in the dissociation curve. It was therefore of interest to ascertain whether variations in the salt content, that is to say, in the concentration of ions other than $\overset{+}{H}$ or $\overline{OH}$, had any effect upon the reduction velocity constant. In the case of the present reaction it was somewhat difficult to obtain clear-cut evidence, on account of the fact that the reduction necessitates the presence of sodium hydrosulphite, *i.e.* of sodium ions and hydrosulphite ions. Experiments showed, however, that as long as the P_H of the mixed solution was kept constant, no alteration in k was brought about either by (i) wide variations in the concentration of sodium hydrosulphite (within the limits stated in § 4), or by (ii) wide variations in the concentration of the buffer constituents. Thus in certain experiments the dilution of the buffer

mixture to one-tenth of its usual strength made no detectable difference in k; or by (iii) replacing one buffer mixture by another of different chemical composition at P_H's, where the effective ranges of the two different buffers overlap.

On these grounds we are inclined to believe that the effect of salts disappears at the low concentrations of hæmoglobin used in our experiments, and that the dominant factors are hydrogen ion concentration and temperature. This conclusion agrees with that which has already been arrived at by Loeb (19) in his study of the physical properties of dilute (1 per cent.) gelatin solutions.

Our thanks are due to the Medical Research Council for defraying in part the expenses involved in this research.

Summary.

1. These experiments on the rate of reduction of hæmoglobin were found to require a very rapid and efficient method of mixing two solutions together, one containing the oxyhæmoglobin, the other a suitable reducing agent. The apparatus devised for this purpose is capable of application to the measurement of other chemical reactions, and has been fully described in a separate paper.

2. The chemical composition of the solution at any required instant after mixing was ascertained by spectroscopic analysis of the fluid as it flowed with uniform velocity from the mixing chamber of the apparatus down a glass observation tube. This analysis was performed by the reversion spectroscope using an auxiliary trough containing a solution of hæmoglobin saturated with carbon monoxide.

3. The reducing agent to be suitable for these experiments must be capable of removing oxygen in solution very rapidly, while it attacks very slowly or not at all the oxygen still in combination with the hæmoglobin. Under these conditions the velocity of the dissociation of oxyhæmoglobin observed will not be appreciably retarded by any back reaction between oxygen and reduced hæmoglobin.

The substance $Na_2S_2O_4$ proved to possess the required chemical properties. The evidence on which this statement is based was obtained in three different ways, namely, by varying the concentration (*a*) of the reducing agent; (*b*) of the oxygen in solution; (*c*) of the oxyhæmoglobin.

4. The velocity of reduction brought about by the chemical reducing agent has been compared with that produced directly by suitable physical

means. It was found that the velocities obtained were practically identical with one another. This is additional evidence that the reducing agent has no direct action on the oxyhæmoglobin, but behaves in the manner stated in the previous paragraph.

5. Our measurements on the velocity of reduction show that a linear relationship exists between the logarithm of the percentage of oxyhæmoglobin and the time during which the reaction has proceeded. We find that this fits in with what would be expected if hæmoglobin obeyed the law of mass action, and that the reduction of oxyhæmoglobin is a mono-molecular reaction.

6. Hydrogen ion concentration has a marked effect on the velocity of the reaction. On the alkaline side of P_H 7·7 the velocity is constant, and on the acid side of P_H 6·3 the velocity is probably also constant, having about seven times the rate found at P_H 7·7; further, between P_H 6·3 and P_H 7·7 there is a gradual change from the one rate to the other.

The interpretation of the P_H effect, and the legitimacy of adopting a single velocity equation are discussed in detail.

7. Temperature also profoundly affects the velocity of the reaction. The temperature coefficients were measured both at P_H 6·3 and at P_H 7·7, and were found in both cases to have the high value of 3·8.

We also found in both cases that the logarithm of the velocity constant plotted against the reciprocal of the absolute temperature gave a straight line relationship as should be the case according to Arrhenius' equation.

8. Variations in the salt content of the solution were found to have no effect on the velocities of the reduction.

The effect of salts upon hæmoglobin probably disappears when the concentration of hæmoglobin is reduced to the extent prevailing in our experiments.

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Some Refractive Indices of Benzene and Cyclohexane.

By Lieut.-Col. J. W. Gifford, F.R.A.S., with an Introduction by Prof. T. M. Lowry, F.R.S.

(Communicated by Prof. T. M. Lowry, F.R.S. Received August 2, 1923.)

I. Introductory.

During the past twenty years the study of Optical Rotatory Dispersion has revealed the fact that the rotatory powers of the vast majority of optically-active substances can be expressed* either by the "simple" Drude equation

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

or by the "complex" equation

$$\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2}.$$

As a result of this investigation it has been possible to disentangle the two factors of rotatory power and rotatory dispersion, and to study the influence of chemical constitution and of physical conditions upon them separately. Moreover, it has been possible in certain classes of compounds to draw important distinctions between substances which exhibit "simple" and those which exhibit "complex" rotatory dispersion.

In dealing with refractive indices, however, no corresponding analysis has been made; and although chemists have measured vast numbers of refractive indices for the D-line of sodium (corresponding with the many

* *See*, for instance, the Bakerian Lecture of 1921 ('Phil. Trans.,' A., vol. 222, pp. 249–308, and in particular p. 257).

measurements of rotatory power made with light of this wave-length), and have even recorded also the refractive indices for the C F and G lines of hydrogen, these data have represented only casually-selected points on curves of unknown form. As a result, tables of "atomic refractions" calculated on this most unsatisfactory basis have fallen into disrepute, since different authors have assigned totally different values to the various elements; and in many cases a whole series of values have been assigned to the same element in different states of combination—quite possibly because these give rise to products of unequal dispersive power.

From this point of view it was clearly a matter of urgency to do for refractive dispersions what had already been done for rotatory dispersions, namely to analyse the forms of the dispersion-curves, to classify them, and to see whether independent constants of refractive power and dispersive power could be calculated from the experimental data. In doing this, however, it was obvious that the mathematical analysis should be carried out on accurately determined numbers, and over the widest possible range of wave-lengths. For this reason the type of observations which have been commonly made in the past, *e.g.* with the Pulfrich refractometer, appeared to be totally inadequate, since they are confined to the visible spectrum and cannot be extended to the even more important ultra-violet region; moreover, they are not of a very high order of accuracy. Direct measurements with a hollow prism, by the methods already described in the case of water ('Roy. Soc. Proc.,' A., vol. 78, p. 406 (1906)), do not suffer from these disadvantages, since by using a fluorescent eyepiece readings can be taken up to the limit of transmission of the medium and of the quartz plates used to contain it; moreover, the accuracy of reading is greater than in instruments of the total-reflexion type.

The present communication represents a first attempt to elucidate this problem. The two substances selected were benzene, C_6H_6, and cyclohexane, C_6H_{12}, which differs from benzene only in that the aromatic ring has been reduced to a cycloparaffin ring by the addition of six atoms of hydrogen. These two substances were selected, not only on account of the simple chemical relationship between them, but also because of their convenient physical properties. Thus each compound, although liquid at ordinary temperatures, freezes above the melting-point of ice, and can, therefore, be freed from all but isomorphous impurities by cooling, crystallising, and draining the crystals in a centrifuge. By adopting this method of purification, and continuing until the melting-point of the compound is constant, a sufficient guarantee of the purity of the products can be obtained.

The wave-lengths selected for the measurements, especially in the ultra-violet region, are of some importance. From a theoretical standpoint, ideal lines to use would be the iron lines of the International Series which are known to seven significant figures; but from the practical aspect of securing measurements with a fluorescent eye-piece, the cadmium lines are far more convenient, since they are more intense and fewer in number, and are therefore easier both to read and to recognise. It is unfortunate that, whilst the three principal wave-lengths in the visible spectrum of cadmium have been measured to eight figures, those of the ultra-violet do not appear to have been measured by the interferometer method, and are therefore known only to a much lower standard of accuracy. Since, however, an error of 0·35 A.U. would be required to alter the refractive index of cyclohexane by 0·00001 even at the extreme limit of transmission, it was considered that the present degree of accuracy in the recorded wave-lengths would be sufficient to test the form of the curves of refractive dispersion. Moreover the gap in our knowledge of the wave-lengths of the ultra-violet lines of cadmium is so obvious, that it must surely be made good before long; and if it should prove that the errors of wave-length are proportionately greater than the errors in the refractive indices now recorded, the effect would probably be to diminish rather than increase the differences shown in the table of data set out below.

It was anticipated that, just as "simple" rotatory dispersion can be expressed by one term of Drude's equation (containing two arbitrary constants, one of rotation and one of dispersion), so the refractive-dispersion of the simpler types of compounds might be expressed by a simple equation of the form

$$n^2 = k_1 + \frac{k_2}{\lambda^2 - \lambda_0^2}$$

containing three arbitrary constants. This expectation was actually realised in the case of cyclohexane, which has a very low dispersion, as may be seen by referring to Table I below; but it was found to be quite impossible to fit the curve for benzene, which has a higher dispersion, in a similar manner.

This contrast is instructive, since cyclohexane is a saturated compound, of a very inert character, highly transparent, and yielding no absorption bands even in the ultra-violet region of the spectrum.* The optical properties of benzene, on the other hand, are singularly complex. Corresponding with the many formulæ which have been assigned to the compound, and to its complex

* A broad band was detected, at wave-length 2520 A.U., in one sample of mother-liquor; but this disappeared on further purification.

chemical character, its absorption spectrum shows not less than seven absorption bands. Even if all these do not influence the refractive indices, it is clear that a considerable series of terms might be required to express the refraction, since each absorption-band represents a possible term in the equation, the value of λ_n being given by the head of the absorption-band in question. In this case, therefore, no real agreement with a simple equation could be anticipated; but it was always possible that a curve of quasi-hyperbolic form might be fitted fairly closely by an equation of similar character containing three arbitrary constants, even if the true equation of the curve were totally different. Actual trial has proved that this is *not* possible in the case of benzene;* and this fact provides clear evidence that the close fit obtained in the case of cyclohexane is not accidental, but is due to a real concordance between the forms of the observed and calculated curves.

II. Experimental.

The refractive indices of benzene have been measured by many observers including Gladstone, Brühl, Jahn, van der Willigen, Röntgen and Simon. Of these van der Willigen and Simon alone appear to have made of them a systematic series. The refractive indices of cyclohexane, C_6H_{12}, have been measured by Eisenlohr (Landolt's 'Physikalisch-Chemische Tabellen,' p. 1031) for the C D F and G lines, probably with a Pulfrich refractometer; but no ultra-violet measurements appear to have been made.

1. *Materials.*—These were supplied by Prof. T. M. Lowry. They had been purified as follows:—

(*a*) *Benzene.*—Five litres of benzene were shaken out with concentrated sulphuric acid until free from thiophen. The product was washed, dried and fractionally distilled. It was then frozen, the "initial" and "final" freezing points being noted as in the purification of acetic acid (Bousfield & Lowry, 'Trans. Chem. Soc.,' vol. 99, p. 1437 (1911)). The liquid residue remaining in the cavity when the "final" freezing-point was determined was poured away, the frozen benzene was allowed partially to melt, and the "mush" of solid and liquid was drained in a silver-plated centrifuge. The drained benzene snow was removed from the cage of the centrifuge, allowed to melt

* Compare S. S. Richardson ('Phil. Mag.,' vol. 31, p. 249 (1916)) who used an equation containing *four* independent variables to express the refractive index of benzene from 1·850 to 0·2837μ, but found a series of differences three times as large as in the case of cyclohexane and apparently systematic in character—negative in the visible region, but positive in the ultra-violet and infra-red.

partially and again drained. A sample of the product then gave a freezing-point of 5·54°. It was melted, allowed to stand over sodium for 24 hours, and fractionally distilled, a small initial and final fraction being rejected. The fully-purified product boiled at 80·2° C. under 768 mm. pressure, and froze at 5·58°.

(*b*) *Cyclohexane.*—A quantity of pure cyclohexane was frozen and the "initial" and "final" freezing-points taken, as in the case of benzene. The solid was then allowed to melt partially and the liquid portion was drained off. The centrifuge could not be used on account of the difficulty of making a satisfactory "mush" of the fine crystals and liquid. The initial and final freezing points of the drained crystals were again taken, and the process repeated. The following figures show the progress of the purification :—

Initial freezing point ..	6·10°, 6·12°, 6·21°, 6·25°, 6·25°, 6·28°.
Final freezing point ..	5·90°, 5·91°, 6·01°, 6·10°, 6·15°, 6·20°.

The product melting at 6·28° was used for the first measurements of refractive indices. Later, a second fraction from the same process of purification was used. The purity of this sample was checked by actual measurements of refractive indices, which were found to be identical with those of the first fraction.

The freedom of this product from benzene was determined by dissolving 0·1945 gms. in 50 c.c. of absolute alcohol, and taking a photograph of the ultra-violet spectrum of iron through it. Even in the thickest layer of liquid (20 cms.) no trace of any absorption bands due to benzene could be noticed, and in a series of nine photographs, taken through different thicknesses of the solution, no trace of absorption could be found. The experiment was repeated with 0·2197 gms. of cyclohexane in 50 c.c. of absolute alcohol. Here again nine photographs taken through different thicknesses of the solution showed equal transparency throughout the spectrum of iron, thus proving the absence of benzene in the sample.

When examined in bulk in the hollow prism on the spectrometer, the absorption began earlier and was more gradual in cyclohexane than in benzene.

2. *Method of observation.*—The containing prism was the hollow quartz prism of 60° used before for the refractive indices of water and then fully described ('Roy. Soc. Proc.,' A., vol. 78, p. 406 (1906)). But although with water there was no apparent leakage from the prism when full, both benzene and cyclohexane escaped in sufficient quantities to attack the rubber bands used to retain the quartz plates, and soon rendered them inoperative. It was, therefore, found necessary to attach the three polished quartz sides to the

body of the prisms by means of glycerine jelly, which entirely met all difficulty. The method of measurement then was as already described ('Roy. Soc. Proc.,' vol. 70, p. 329 (1902)).

3. *Instruments.*—These were the same as were used for the measurements of the refractive indices of water (*loc. cit.*), with the difference that both instruments are now provided with objectives of fluorite corrected by quartz. The difficulties of collimation are thus greatly reduced.

4. *Temperature.*—A standard thermometer was used as before (*loc. cit.*), but owing to the large temperature refraction coefficient (dn/dt) in both substances, the help of a reading microscope became necessary. With this microscope the temperature of the prism could be recorded within approximately 0·02° C. or less. This point plays a very important part in determining the accuracy of the measurements.

5. *Pressure.*—The system of correction for atmospheric pressure already described ('Roy. Soc. Proc.,' vol. 100, p. 621 (1922)) has been applied.

6. *Accuracy.*—Greater accuracy than that claimed for the refractive indices of water (*loc. cit.*) is not demanded. All the indices except those for wave-lengths 3250 and 2981 in benzene and those for 3281 and 3250 in cyclohexane were measured visually, those in the ultra-violet with a fluorescent eyepiece. Those excepted were not measurable by the eye even with the fluorescent eyepiece, and had to be observed photographically. But since the objectives used had a focus of 30 inches, distortion was at a minimum. The index of the mean D line for benzene is given by Dufet for 15 observers at 20° C. (Dufet, 'Données Numériques,' vol. 1, p. 105); the mean of all these figures is 1·50127. The index given in the table reduced to 20° C. by the refraction temperature coefficient interpolated for D is 1·50129.

For the purpose of the temperature-refraction coefficients which follow, three exceptionally bright lines were chosen.

Wave-length and element	He 7065 (B′)	Fe 5270 (E)	He 4472
T.R. coefficient benzene	−0·0006357	−0·0006674	−0·0006708
T.R. coefficient cyclohexane ..	−0·0005376	−0·0005515	−0·0005647

From these, coefficients for other wave-lengths were interpolated in proportion to the indices, and the refractive indices in the table corrected accordingly.

The refractive indices, reduced to a uniform temperature of 15° C., are set out in Table 1, together with the differences between the observed values for cyclohexane and those calculated from the formula

$$n^2 = 2\cdot011046 + \frac{0\cdot0102467}{\lambda^2 - 0\cdot013977}.$$

Table I.—Refractive Indices.

Line.	Wave-length.		Benzene.	Cyclohexane. Observed.	Cyclohexane. Calculated.	Cyclohexane. Difference.	Temperature-Coefficient.
A′	Kα	{7701·92, 7668·54}	1·494534	1·424343	1·42436	−0·00002	−0·00053493
B′	He	7065·200*	1·497005	1·425544	1·42554	0·00000	−0·00053755
	Li	6707·846*	1·498913	1·426422	1·42634	+0·00008	−0·00053955
C.	Hα	6563·05	1·499659	1·426732	1·42675	−0·00002	−0·00053994
D.	Na	{5889·965*, 5895·932*}	1·504551	1·429001	1·42891	+0·00009	−0·00054518
Λ	Pb	5608·0	1·506982	1·430114	1·43010	+0·00001	−0·00054764
	Hg	5460·742*	1·508506	1·430840	1·43077	+0·00007	−0·00054924
E.	Fe	{5270·353, 5269·532}	1·510714	1·431800	1·43174	+0·00006	−0·00055145
F.	Hβ	4861·50	1·516392	1·434314	1·43427	+0·00004	−0·00055726
Φ	Cd	4678·37	1·519640	1·435761	1·43564	+0·00012	−0·00056073
	He	4471·482*	1·523856	1·437410	1·43741	0·00000	
	Cd	4413·23	1·524983	1·438024	1·43796	+0·00006	−0·00056610
G′.	H	4340·66	1·526963	1·438815	1·43867	+0·00014	−0·00056803
	Hg	4046·78	1·535042	1·442195	1·44203	+0·00016	−0·00057590
	Cd	3610·66	1·552157	1·448690	1·44882	−0·00013	−0·00059160
	Cd	3466·33	1·560503	1·451740	1·45174	0·00000	−0·00059909
	Cd	3403·74	1·564470	1·453218	1·45314	+0·00008	−0·00060252
	Zn	3345·13	1·568701	1·454380	1·45454	−0·00016	−0·00060533
	Zn	3302·80	1·571391	1·455550	1·45560	−0·00005	−0·00060806
	Zn	3282·50	1·572863	1·456132	1·45613	0·00000	
	Cd	3261·17		1·457915	1·45670	+0·00121	
	Cd	3252·65	1·579968	1·458230	1·45693	+0·00130	
	Cd	2980·75	1·589904 absorption.	absorption			

* Secondary Standard.

The average difference for 20 wave-lengths is 0·00006. In the last two wave-lengths, however, the differences are much larger, and appear to indicate a real deviation from the formula as the limits of absorption are approached.

My thanks are due to Prof. Lowry for suggesting the subject of research, providing and describing the material, and communicating the paper, and by no means least to my wife for drawing the curves for checking the work.

Crystal Structure and Chemical Constitution of Basic Beryllium Acetate and Propionate.

By Sir William Bragg, F.R.S., and Gilbert T. Morgan, F.R.S.

(Received October 6, 1923.)

The co-ordination theory of molecular structure postulates the existence for each valent chemical element of an integer representing the maximum number of associating units which can be grouped around the atomic sphere of the element. This so-called "co-ordination number" varies with the atomic volume of the element, and although in the case of elements of medium atomic volume the number is generally six, yet with elements of small atomic volume this number is diminished to four or even less.

This conception of co-ordination was elaborated by Alfred Werner into a comprehensive theory of chemical combination and molecular structure long before the electronic constitution of chemical atoms had been revealed, but nevertheless the co-ordination theory has been shown to accord with many of the new facts since discovered by infra-atomic investigations and by X-ray analysis.

Considerable success has already attended the application of X-ray measurements to the study of the crystals of co-ordination compounds. Last year Wyckoff showed in this way that in the hexamminonickel halides, NiX_2, $6NH_3$ (where X = Cl, Br or I), all six of the ammonia molecules must be alike and related in the same manner to a central nickel atom to which they approach more closely than to any other atoms of the compound. This investigator concludes that it is entirely appropriate to write the formula of these compounds in the customary co-ordination manner [Ni, $6NH_3$] X_2

('J. Amer. Chem. Soc.,' vol. 44, p. 1244 (1922)). It must be admitted that this experimental evidence is a remarkable confirmation of the validity of Werner's conception of the co-ordination sphere.

By the X-ray measurements of crystals of ammonium platinichloride, Wyckoff and Posnjak (*ibid.*, vol. 43, p. 2308 (1921)) showed that this salt has a structure like that assumed for calcium fluoride if platinichloride radicals, $PtCl_6$, replace the calcium atoms, and if NH_4 groups are introduced in place of fluorine atoms. These results furnish a physical demonstration of the existence as separate entities of the three co-ordination nuclei of this platinichloride $[NH_4]_2 [PtCl_6]$. Wyckoff has also by X-ray analysis thrown light on the constitution of cæsium dichloroiodide, a substance in which co-ordination occurs round the anion $Cs[ICl_2]$ (*ibid.*, vol. 42, p. 1100 (1920)). Cæsium dichloroiodide has also been investigated by G. L. Clark ('Proc. Nat. Acad. Sci.,' vol. 9, p. 117 (1923)), who has determined the crystal structure of this salt and of its analogues, in which iodine and bromine replace the chlorine atoms. His results indicate that the halogen atoms constitute a singly acting group as in the formation of complex ions in solution.

In connection with co-ordinated anions reference should be made to the work of W. L. Bragg on the isomorphous pair, $NaNO_3$, and $CaCO_3$, which on the ordinary theory of fixed valency constitutes one of the anomalies of Mitscherlich's principle of isomorphism. The X-ray analysis of the crystals affords experimental support to the co-ordination hypothesis which attributes a similar structure to the two isomorphs,

$$\mathrm{Na}\left[\begin{array}{c}\mathrm{O}\\ \mathrm{N}\\ \mathrm{O}\quad\mathrm{O}\end{array}\right] \qquad\qquad \mathrm{Ca}\left[\begin{array}{c}\mathrm{O}\\ \mathrm{C}\\ \mathrm{O}\quad\mathrm{O}\end{array}\right]$$

with the same spatial arrangement of the two pairs of four atoms which make up the two anions ('Roy. Soc. Proc.,' A, vol. 89, p. 468 (1914)).

In all probability, atomic volume and co-ordination number are both closely connected with the electronic structure of atoms, for elements of simple structure possess relatively small atomic volumes and low atomic numbers.

Falling within this category are the elements of the first short period of the natural classification, namely, the series beginning with lithium and ending with fluorine. These elements exhibit co-ordination numbers which do not usually exceed four and are sometimes less. A possible exception to this generalisation occurs in the borotungstates $[B\,(W_2O_7)_6]\,X'_9$, complex compounds of boron, in which this element appears to have a co-ordination number of six, although

in the great majority of its inorganic and organic derivatives boron has a co-ordination index of four (Pfeiffer, 'Zeitschr. anorg. Chem.,' vol. 105, p. 26 (1918); Werner, 'Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie,' p. 148 (1920)).

The case of the neighbouring element, beryllium, which merits further attention, is the subject of the investigation described below.

Among the simpler inorganic compounds of this metal one finds the following: $BeCl_2$, $4H_2O$; $Be(ClO_4)_2$, $4H_2O$; $BeSO_4$, $4H_2O$ and K_2BeF_4, the compositions of which suggest that the co-ordination number is four. A similar indication is furnished by the organic compound, beryllium acetylacetone, $Be(C_5H_7O_2)_2$, in which each diketonic complex, $C_5H_7O_2$ or $CH_3.CO.CH.CO.CH_3$, functions as two associating units.

One of the outstanding features of the chemistry of beryllium is the tendency for this metal to form basic salts with the volatile inorganic and organic acids. Of the basic beryllium salts with acids of the acetic series a remarkable group exists, the members of which have the general formula $Be_4O(RCO_2)_6$, where R is either hydrogen in the basic formate or an alkyl group in any of the homologues of this salt. The higher members of the group are oily, the lower members, with the exception of the basic formate, have been obtained crystalline and are amenable to X-ray analysis.

These organic beryllium compounds are practically insoluble in water, but with the exception of the formate, they dissolve readily in anhydrous organic solvents. In their solubility in non-ionising media these compounds differ essentially from the majority of normal metallic salts of organic acids. Moreover, when solid the beryllium derivatives have definite melting points, and they can be distilled without decomposition under diminished pressure. The vapour density of the basic acetate has been determined (Urbain and Lacombe, 'Compt. Rend.,' vol. 133, p. 875 (1901); vol. 134, p. 773 (1902)), and it agrees closely with the value calculated for the undissociated compound of formula $Be_4O(CH_3.CO_2)_6$. Throughout this group of beryllium compounds there is no sign of either hydrolytic or ionic dissociation except under conditions involving complete disruption of the molecule.

These remarkable physical and chemical properties do not lend support to the formulation of basic beryllium acetate as a molecular compound, $3Be(CH_3.CO_2)_2$, BeO, but they point to a unitary structure for the basic acetate similar to that ascribed to non-ionised organic compounds.

At the Australian meeting of the British Association (Melbourne, 1914) one of us (G.T.M.) suggested for basic beryllium acetate a plane formula

(fig. 1), in which this unitary conception of the structure is combined with the hypothesis of a maximum co-ordination number, four, for beryllium.

Further consideration of the problem, however, led to the view that in this extremely stable compound a more symmetrical arrangement is probably present. This greater symmetry would be attained by placing the unique oxygen atom at the centre of a tetrahedron, the four beryllium atoms at or near the vertices of this solid, with the six acetate groups spanning the edges of the tetrahedron as in fig. 2.*

This symmetrical arrangement of the constituent parts of the basic acetate

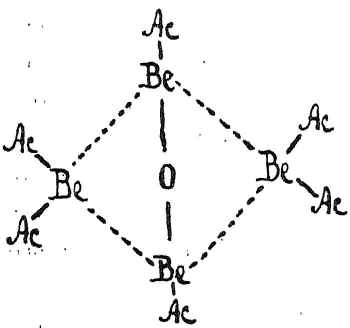


Fig. 1.

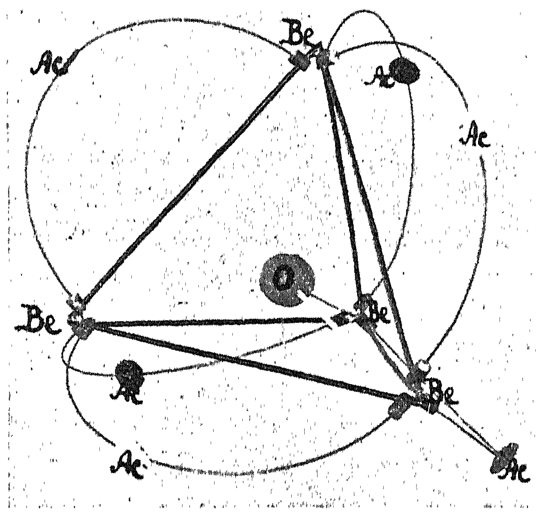


Fig. 2.

molecule is capable of simple interpretation in terms of the electronic theory of valency.

Each of the four beryllium atoms possesses two peripheral or valency electrons making eight in all, and when the four bivalent atoms enter into combination with the other constituents of the acetate molecule the distribution of these eight electrons completes the octet of the unique oxygen atom, and also completes those of the oxygen atoms of the six acetate radicals. In this distribution of electrons two pass to the unique oxygen atom and one to each of the six acetate groups.

* In the course of private discussion it was found that this idea had occurred independently to Mr. A. Berry (Aberystwyth) and to Dr. J. D. Main Smith (Birmingham) on the basis of co-ordination and to Mr. T. V. Barker (Oxford) on crystallographic grounds. Compare also Sidgwick, *Nature*, vol. 111, p. 808 (1923).

Dealing first with the unique oxygen it will be seen that this atom now having eight peripheral electrons resembles neon in its outer form, and is, therefore, nonvalent in a chemical sense. But it differs from the inert gas in being negatively charged ($-2e$) and is accordingly able to exert an electrostatic force attracting to its centre positively charged ions. The four beryllium ions having lost their peripheral electrons now resemble helium as regards their outer form, and like this inert gas they are nonvalent, although they differ from helium in being positively charged ($+2e$). Hence these four beyllium ions are attracted by the unique oxygen, and their mutual repulsions cause them to assume a tetrahedral arrangement round the sphere of influence of this central atom.

The four positively charged beryllium atoms can themselves attract negatively charged ions. The twelve oxygen atoms of the six acetate groups having completed their respective octets are also nonvalent like neon, but differ from this gas in being negatively charged. Three of these acetate oxygens are attracted to each beryllium ion making with the central oxygen atom subsidiary tetrahedral arrangements round each beryllium atom. The carbon nuclei of the six acetate groups become arranged symmetrically along the edges of the main tetrahedron as shown in fig. 2. It is to be expected that the acetate group will undergo modification of its internal structure in consequence of its inclusion in the molecule and in the crystal.

This tetrahedral structure is highly developed in the molecule of the basic acetate inasmuch as no less than eleven tetrahedra can be distinguished as follows: The central tetrahedron round the unique oxygen atom, four tetrahedra round the beryllium atoms and the six tetrahedral carbon atoms of the six methyl groups.

These speculations concerning basic beryllium acetate have now been put to the test of X-ray analysis with the result that the earlier plane formulation (I) has been disproved, whereas the tetrahedral configuration (II) has been fully substantiated.

The completely symmetrical arrangement of acidic groups along the edges of the tetrahedron is possible only in the case of the basic formate or acetate, and this symmetrical distribution of the component atoms of the acetate group manifests itself in the crystalline structure of basic beryllium acetate which belongs to the cubic system.

When, however, the acetate groups are replaced by propionate complexes, as in basic beryllium propionate, the symmetrical arrangement is no longer possible. This decrease in molecular symmetry is also revealed in the

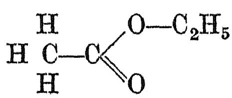
crystallographic examination and X-ray analysis of the crystalline propionate which belongs to the monoclinic prismatic class.

The same loss of molecular symmetry is apparent in the basic beryllium acetate-propionate which, however, has so far been examined only in powder form owing to the difficulty of obtaining large crystals.

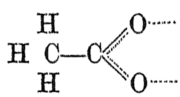
The Co-ordination Formula for the Acetate Group.

The results of X-ray analysis confirm in a remarkable manner the formulation of the acetate group on a co-ordination basis.

Although the presence of a carbonyl group in ethyl acetate (III) is revealed by the action of zinc alkyls or the Grignard compounds, these reagents fail to detect carbonyl in the molecule of acetic acid or its metallic salts (IV). This difference is in all probability associated with a definite change of chemical structure. In the esters the carbonyl group retains its integrity and unsaturated character as in III, but in the free acid or in the



III.



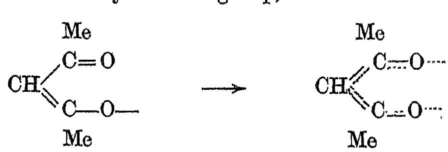
IV.

basic beryllium acetate, the original difference between hydroxylic and carbonyl oxygens has been smoothed out so that the co-ordinated acetate group has now become symmetrical in the sense demanded by X-ray analysis.*

Preparation of Basic Beryllium Acetate and its Homologues.

The beryllium hydroxide employed as the starting point in these preparations was obtained from American beryl, which was decomposed by sintering with sodium silicofluoride (Copaux, 'Compt. Rend.,' vol. 168, p. 610

* According to some recent experiments made by Mr. Astbury the X-ray analysis of aluminium and gallium acetylacetones proves that there is a plane of symmetry in the molecule and in the acetylacetone group, which points strongly to a smoothing out of differences between carbonyl and enolic oxygen and leads to the establishment in these compounds of a symmetrical acetylacetone group,



as predicted by one of us and H. W. Moss from the co-ordination view-point in 1914 (*Trans. Chem. Soc.*, vol. 105, p. 193 (1914)).

(1919)), the purification of beryllia from alumina being effected by separating the soluble sodium beryllium fluoride from the sparingly soluble sodium aluminium fluoride and by the solubility of beryllium in aqueous ammonium carbonate.

Basic beryllium acetate $Be_4O(CH_3.CO_2)_6$ was prepared by dissolving beryllium hydroxide in 50 per cent. acetic acid, evaporating to dryness and crystallising the residue repeatedly from chloroform until the melting point remained constant at 285–286° (the highest recorded value being 283–284° (Lacombe, 'Compt. Rend.,' vol. 134, p. 773 (1902)).

The purity of the specimen was confirmed by analysis. [Found C = 36·06, H = 4·44, Be = 8·73. $C_{12}H_{18}O_{13}Be_4$ requires C = 35·43, H = 4·43, Be = 8·96 per cent.]

Basic beryllium propionate, $Be_4O(CH_3.CH_2.CO_2)_6$, prepared by dissolving beryllium hydroxide in propionic acid, was crystallised from light petroleum (b.p. 80–100°) until the melting point remained constant at 133–135°; the melting point for this compound has hitherto been recorded as 119–120° (Lacombe, *loc. cit.*).

The following analytical data confirm the purity of the specimen [found C = 43·94, H = 6·11, Be = 7·59, 7·56. $C_{18}H_{30}O_{13}Be_4$ requires C = 44·04, H = 6·12, Be = 7·43 per cent.]. The yield of propionate was 82 per cent. For the following measurements, large crystals were prepared by allowing a solution of the compound in propionic acid to evaporate spontaneously.

Basic beryllium acetate-propionate, $Be_4O(CH_3.CO_2)_3.(CH_3.CH_2.CO_2)_3$, was prepared by heating in a reflux apparatus for $1\frac{1}{2}$ hours 14 gms. of basic propionate and 25 c.c. of acetyl chloride. The greater part of the propionate was then transformed into the mixed compound. Excess of acetyl chloride was removed *in vacuo* at the ordinary temperature. The product was separated from basic acetate and unchanged propionate by repeated crystallisation from light petroleum (b.p. 80–100°). The mixed acetate-propionate separated in felted masses of needles sintering at 139° and melting at 140–142°, the recorded value being 127° (Tanatar and Kurowski, 'J. Russ. Phys. Chem. Soc.,' vol. 39, p. 936 (1907)). The purity of the product was confirmed by analysis: [Found C = 40·33, H = 5·57, Be = 8·13. $C_{15}H_{24}O_{13}Be_4$ requires C = 40·15, H = 5·35, Be = 8·12 per cent.].

The foregoing preparations were employed in the X-ray measurements recorded below.

A crystallographic examination of the basic beryllium acetate made by Mr. T. V. Barker confirmed the fact that this compound is a regular octahedron

geometrically and singly refracting optically. There is no doubt that it belongs to the cubic system, and in regard to symmetry there is no evidence against it belonging to Class 32. The natural etch figures are similar triangles on all the faces, and not tetrahedrally segregated. There is a moderately well developed octahedral cleavage. The specific gravity determined on clear splinters is 1·39 correct to the second decimal place.

Part II. Analysis by X-Rays.

Basic Beryllium Acetate.

The structure of basic beryllium acetate is of peculiar interest on account of its own characteristics as well as on account of its chemical significance. It resembles the structure of the diamond, the acetate molecule replacing the carbon atom. This will be clear if the figures in the first table are considered in connection with the following rules of interpretation of X-ray results.

In the simple cubic lattice the crystal unit of pattern is a cube formed by joining together eight neighbouring points of the lattice. A point may represent any group of atoms, but every point in any one crystal must represent a group identical in all respects including orientation. The unit cell then includes, as it should do, the substance of one group. The general form of the (lmn) plane referred to the edges of one of the cubes as axes is $lx + my + nz = 2pa$, where $2a$ is the edge of the cube and p is any integer. The perpendicular from the origin on the plane is $2pa/\sqrt{(l^2 + m^2 + n^2)}$, and the spacing is $2a/\sqrt{(l^2 + m^2 + n^2)}$. By giving lmn all possible integral values we form a list of all possible spacings: the largest spacings being usually the most interesting and the most easily observed. Such a list is given by Hull ('X-Ray Studies,' p. 189).

The face centred cubic lattice may be derived from the simple lattice by placing an additional point, representing the same group as before, at the centre of each cube face. The cube now contains the substance of four groups. The crystal unit cell is not now the cube itself, but the equal-sided rhomb formed by joining together the six face centres and any two corners of the cube which lie at opposite ends of a diagonal ('X-Rays and Crystal Structure,' p. 57).

It is still convenient to use the cube as a frame of reference; so that we may draw up a list of the spacings of the new lattice by striking out of the former list such as are no longer possible. The original list is to be reduced because the introduction of the new points into the old lattice has halved a number of

the original spacings. It can be readily shown that the spacings of the simple cube are unaffected by the addition of the new points if the indices of the corresponding planes are all odd or all even. For if $l + m$, for example, were odd, then the result of substituting the co-ordinates of a face centre such as $(a\ a\ o)$ in the expression $lx + my + nz$ would be to make it an odd multiple of a, whereas for all the old points the expression $= 2pa$, an even multiple of a. The (111) and (113) spacings are still in the list, but not the (100), nor the (112). So also the (224) is to be found, in the sense that though the first order reflection from (112) has gone, the second order remains. The halving of all but the "all-odd" or "all-even" spacings is the characteristic feature of the face-centred lattice, and is to be found, for example, in rock salt.

The diamond arrangement is obtained from the face-centred cube lattice by giving the latter a translation along a cube diagonal equal to a quarter of the length of the diagonal, thus adding four more points to the cube content. The arrangement is then such that every point is at the centre of gravity of four others. If all these points are supposed to have equal effects on the X-rays we have a new set of spacings, which, it may be shown, can be obtained from the face-centred set by striking out all spacings for which $l + m + n = 4p + 2$, where p is an integer. A full list has been given by Hull (*loc. cit.*).

It is not to be expected, however, that this set will ever be found to exist, because the diamond arrangement is not a true lattice. There are two kinds of representative points in it: the two kinds of group which are represented face opposite ways and may therefore be expected to differ in their action on X-rays. The differences in the case of diamond itself are very small, and were overlooked in the early measurements. Later it was shown that a (222) reflection really existed, though (222) is one of those for which the sum of the indices $= 4p + 2$.

We ought not, in fact, to look upon the new set of points, the addition of which has led to the diamond arrangement, as due to a translation from the original set, and consequently there is no "diamond lattice," correctly speaking. It happens that in the case of diamond the spacings actually found are very nearly those of the "diamond arrangement"; which suggests that the carbon atoms are very nearly but not quite spherical. It is natural to suppose that the departure from the sphere is towards the regular tetrahedron; and, further, that the tetrahedron which represents the behaviour of the carbon atom is placed so that the centre of each of its four neighbours lies on one of the lines joining the centre of the tetrahedron to a vertex. Two

neighbouring tetrahedra face each other, vertex to vertex. There are two kinds of orientation of the one kind of tetrahedral atom: they face each other along any diagonal of the cube. One kind is the reflection of the other, with a necessary shift, in any cube face. Every tetrahedron edge is parallel to a diagonal of a cube face.

We are led to consider how the list of face-centred spacings is to be modified if the points of the diamond arrangement represents tetrahedral atoms or groups of atoms which differ in orientation and in nothing else. We may represent a tetrahedron by its vertices.

If we imagine ourselves to be looking through the cube in a direction parallel to one edge, we should see the arrangement of points represented in the figure, the two nearer corners of each tetrahedron being represented by dots and the two further by small circles. The unseen edge of each tetrahedron

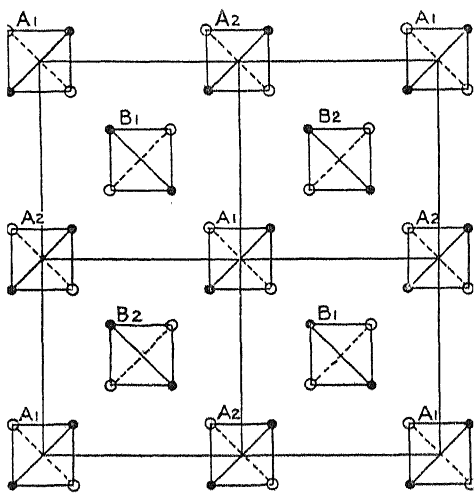


Fig. 3.

is represented by a dotted line. The various centres of tetrahedra do not all lie in the same plane. The centres of those marked A_1 may be considered to be in the plane of the paper. Those marked B_1 lie in a plane which is at a depth $a/2$ below the paper; the next are the A_2 tetrahedra at a depth a; the next those marked B_2 lying at a depth $3a/2$. The next are immediately behind those marked A_1, and are at a depth $2a$.

If the sides of the square are taken as axes of x and y, the axis of z being perpendicular to the plane of the paper, then (lmo) or $lx + my = 2pa$ represents a series of parallel planes perpendicular to the paper and passing through the corners of the square and similar corners: l, m, p are integers and the side of

the square is equal to $2a$. When l and m are both even, the plane is an "all-even" plane, and its spacing is found in the face-centred list.

To all (lmo) planes, when acting as reflectors of the X-rays, an A tetrahedron is indistinguishable from a B tetrahedron; the perpendiculars upon a plane from the four corners of an A are the same as those from a B, provided the perpendiculars from the centres are the same.

The co-ordinates in the plane of the paper of the centres of the B tetrahedra are of the form $ha/2$, $ka/2$, where h and k are both odd numbers. Such points will lie on "all-even" planes $lx + my = 2pa$ only if $l + m$ is a multiple of four. Thus if l, m are any integers we have the various planes of the form (lmo) which belong to the simple cubic lattice: if l and m are even the number is reduced to those that belong to the face-centred cubic lattice, and if the B points are put into the lattice we must further strike out the planes for which $l + m$ is not a multiple of four.

In the last case the planes that are removed from the face-centred list are, so far as the table goes, (200), (420), (600), (640). This sifting applies only to planes passing through an edge of the cubic cell: for the tetrahedra are not equivalent to each other for any other set of planes. For instance, 222, 442 and 622 remain. If the A and B points represented spheres and not tetrahedra these last would disappear also, and we should have the diamond arrangement. In diamond they do very nearly disapppear, because the carbon atoms are almost spherical. In the basic beryllium acetate the molecules represented by the A and B points have a pronounced tetrahedral character and the spacings in question are all found.

The table shows in the first column a list of planes whose spacings are to be found in the face-centred lattice: for each of them l, m, n are all even or all odd. All the spacings are included down to (800), together with (555) and (888). In the second column are placed the spacings of these planes, calculated for a cubic cell of side 15·72; which cell will contain eight molecules, the number required by the hypothetical arrangement of the acetate. This number also gives the correct value of the specific gravity, viz., 1·39.

The third column shows which of these spacings are to be found in the diamond arrangement; those remaining are marked with a cross, and those disappearing with a dash. The fourth column shows the tetrahedral set, which includes some that are not found in the third column.

The fifth column shows the lines which have been observed by the ionisation spectrometer, the figures denoting relative approximate values of intensity. In some cases the spacings have been measured and the results are shown

in the sixth column. The seventh and eighth columns show the results found by the powder method,* and the relative strengths of the lines on the photographic plate; *w*, *m* and *s* stand for weak, moderate and strong respectively, *v* denotes "very."

Plane.	Calculated spacing.	"Diamond."	"Tetrahedron."	Ionisation spectrometer.		Powder method.	
I.	II.	III.	IV.	V.	VI.	VII.	VIII.
111	9·07	×	×	300	9·07	9·07	*v.s.*
200	7·86	—	—	0			
220	5·58	×	×	Trace			
311	4·75	×	×	35	4·73	4·81	*m.w.*
222	4·53	—	×	110	4·53	4·57	*m.w.*
400	3·93	×	×	220	3·92	3·96	*v.s.*
331	3·62	×	×	55	3·60	3·64	*s.*
420	3·52	—	—	0			
422	3·22	×	×	55		3·23	*v.s.*
511	3·03	×	×	Trace		2·97	*v.w.*
333	3·03	×	×	Trace		2·97	
440	2·79	×	×	55	2·81	2·81	*m.s.*
531	2·67	×	×			2·67	*m.*
442	2·64	—	×			2·60	*v.w.*
600	2·62	—	—	0			
620	2·49	×	×	20		2·51	*s.*
533	2·40	×	×			2·39	*m.s.*
622	2·37	—	×			2·39	
444	2·27	×	×	35		2·28	*m.w.*
711	2·21	×	×			2·22	*v.w.*
551	2·21	×	×			2·22	
640	2·18	—	—				
642	2·10	×	×			2·11	*v.w.*
553	2·05	×	×			2·05	*v.w.*
731	2·05	×	×			2·05	
800	1·97	×	×	35		1·95	*v.w.*
555	1·81	×	×	45			
888	1·13	×	×	10			

The above table shows that all the spacings observed by either method belong to the tetrahedral arrangement; and that nearly all the spacings of the arrangement have been found. The general argument is in no way affected by the absence of a spacing that might be found, though it would be by the presence of a spacing that ought not to be found.

The tetrahedron of our hypothesis is regular; and therefore also the molecule of the crystal which we have shown to possess the tetrahedral arrangement is regular. The arrangement of the atoms within the molecule must be such as to give this degree of symmetry. The unique oxygen atom must be at the centre of the tetrahedron, and the four beryllium atoms must lie on the four lines joining the centre to the vertices. An acetate group, or,

* We are indebted to Dr. Shearer for taking the photographs.

more correctly, the atoms composing an acetate group, must be disposed so as to be symmetrical about a plane perpendicular to each tetrahedron edge and passing through the opposite edge.

The intensities of the various reflections have not been considered so far; nor can we interpret them fully since the molecule is complex. The most remarkable points are the great weakness of 220 and the strength of 400 and 222. All these facts fit in with a hypothesis that the influential centres of dispersion are crowded towards the corners of the tetrahedra, the tetrahedra being supposed to be in contact with their neighbours at their corners.

Basic Beryllium Propionate.

This crystal does not appear to have been measured previously. The X-ray measurements show that there are two molecules in the unit cell, and that it probably belongs to the monoclinic prismatic class. The specific gravity is 1·25. The dimensions of the cell are very nearly as shown in fig. 4.

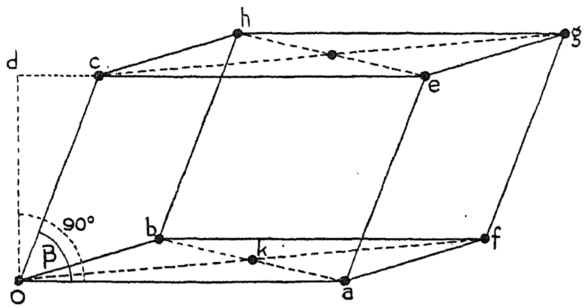


FIG. 4.

$a = 16{\cdot}00$, $b = 9{\cdot}76$, $c = 9{\cdot}15$, $\beta = 116°\ 7'$. If $dOa = 90°$, $cd = ce/4$ very nearly. Assuming these dimensions the calculated values of the spacings of the various planes are as shown in the second column of the following table. The observed values are shown in the third, and the agreement is satisfactory. A number of the angles between the various planes were also measured, and found to agree within a few minutes with the calculated values.

As in naphthalene the second molecule is at the centre of the *ab* face, or very nearly so. If the molecule has a centre of symmetry its position can be exactly defined with reference to the first. It is at once the reflected molecule, and must therefore lie on some line parallel to the *b* axis and passing through the centre of a face of the cell, and at the same time it is the digonal molecule, and therefore lies on a plane perpendicular to the *b* axis and passing through a

face centre. The halving of the (010) spacing proves the latter: the 9·76 spacing was not found by the spectrometer, nor was it recorded on a photograph which Dr. Shearer was good enough to make by the powder method. The former would follow from the halving of all (*l*, *o*, *n*) spacings for which *l* is odd. The table shows that (100) is halved, and that (001), (20$\bar{1}$), (40$\bar{1}$) are not, which is so far correct. The 101 and 10$\bar{1}$ spacings if not halved would be 6·08 and 9·07 respectively. Dr. Shearer's plate shows a line of moderate strength which might be the latter, but which also might be due to the β-ray reflected by the (001) plane; and also a weak line which gives a spacing 6·00. If these are real then the second molecule is not quite the reflection of the first, while at the same time it is derived from the first by a rotation through 180° and a shift. This implies that the molecule of the propionate has actually no symmetry at all, though it is approximately centrosymmetrical. The 101 and 10$\bar{1}$ spacings were not found by the ionisation spectrometer, but a more careful search might be made.

However, the chief point of interest, which is perfectly clear, is that the addition of the CH_2 to the acetate has completely destroyed the symmetry of the molecule as it is built into the crystal. This may be due to the fact that the atoms of the propionate group can no longer be arranged in a symmetrical manner with respect to a plane.

Plane.	Spacing calculated.	Spacing observed.	Intensity.	Lines found by Shearer.
100	14·36	7·18	*m.*	
010	9·76	4·88	*m.*	
001	8·23	8·23	*v.s.*	9·00 *m.* 001β or 10$\bar{1}\alpha$?
021	4·19	4·21	*m.*	8.15 *s.* 001, 110.
043	1·82	1·82	*v.w.*	7·79 *m.w.*
041	2·34	2·34	*w.*	7·26 *m.s.* 100, 20$\bar{1}$.
20$\bar{1}$	7·20	7·20	*s.*	6·70 *m.* 11$\bar{1}$.
40$\bar{1}$	4·00	4·00	*s.*	6·00 *w.* 101?
110	8·07	8·08	*s.*	5·42 *w.* ?
120	4·62	4·66	*s.*	4·26 *m.* 021, 12$\bar{1}$.
310	4·30	4·29	*v.w.*	3·95 *s.* 40$\bar{1}$.
111	5·16	5·16	*v.w.*	
222	2·58	2·58	*w.*	
11$\bar{1}$	6·64	6·61	*m.*	
112	3·35	3·34	*m.s.*	
11$\bar{2}$	4·10	4·05	*m.*	
121	3·80	3·81	*m.*	
12$\bar{1}$	4·30	4·32	*m.*	
41$\bar{1}$	3·70	3·70	*w.*	
42$\bar{1}$	3·09	3·11	*v.w.*	

Basic Beryllium Acetate-Propionate.

The powder photograph shows a set of spacings which are not those of a crystal of high symmetry; but might belong to a structure analogous to the propionate. In the absence of crystals of sufficient size it was not possible to use the spectrometer.

The beryl employed in these experiments was obtained by the aid of a grant from the Department of Scientific and Industrial Research; it was worked up into the purified organic compounds with the assistance of Messrs. T. J. Hedley and C. R. Porter.

An Experiment on the Origin of the Earth's Magnetic Field.

By H. A. Wilson, F.R.S., Rice Institute, Houston, Texas, U.S.A.

(Received July 30, 1923.)

Of the many suggestions which have been made as to the origin of the earth's magnetic field, perhaps the most promising is that it may be due to a slight modification of the laws of electrodynamics from the commonly accepted form.* Electrically neutral matter is believed to consist of an intimate mixture of enormous amounts of positive and negative electricities, the electric and magnetic effects of which are usually supposed to balance each other. If the balance were not quite exact then small residual effects would be expected, among which gravitation and the earth's magnetic field might be included.

On such an hypothesis we might expect moving matter to produce a magnetic field similar to the field due to moving electricity, and we should expect some relation between the magnetic field due to moving matter and its gravitational action.

The gravitational unit of matter (about 4,000 grams), which attracts an equal mass at one cm. distance with a force of one dyne, might be expected to produce a magnetic field of the same order of magnitude as the electrostatic unit of electricity defined in the same way.

* "A Critical Examination of the Possible Causes of Terrestrial Magnetism," by Sir A. Schuster, 'Proc. Lond. Phys. Soc.,' p. 121 (1912); "Unsolved Problems of Cosmical Physics," by W. F. G. Swann, 'Journal of the Franklin Institute,' April (1923).

The magnetic moment of a rotating sphere of electricity is equal to $\frac{4}{15}\rho\omega a^5$, where ρ is its density of charge in electromagnetic units per c.c., ω its angular velocity and a its radius. The field strength at the equator is therefore $\frac{4}{15}\rho\omega a^2$.

In the case of the earth, if we suppose a gravitational unit of matter equivalent to one electrostatic unit, we have $\rho = 5{\cdot}5/(4{,}000 \times 3 \times 10^{10}) = 5 \times 10^{-14}$, $\omega = 7{\cdot}3 \times 10^{-5}$ and $a = 6 \times 10^8$ cms.; so that $\frac{4}{15}\rho\omega a^2 =$ 1 Gauss, nearly, which is about three times the observed horizontal magnetic field at the earth's equator. A similar calculation gives a field at the sun's equator also about three times that observed.

It appears therefore that the assumption that a moving mass produces a magnetic field, like a moving charge of electricity, and that a gravitational unit of matter is equivalent to an electrostatic unit of electricity, leads to magnetic fields for the earth and sun of the right order of magnitude.

The main object of this paper is to describe an experiment made to test such theories of the earth's magnetic field, the result of which seems to be to show that not more than one part in one thousand of it can be attributed to a magnetic effect of moving matter, similar to that of moving electricity.

Consider a unit magnetic pole at the surface of a sphere of matter of radius a. If both are at rest there is no force on the pole. If the pole is at rest and the sphere moving, with velocity v, in a direction perpendicular to the line joining the centre of the sphere to the pole, there will be a force on the pole equal to ev/a^2, where e is the electrical charge equivalent to the mass of the sphere. If both move together with velocity v then the principle of relativity requires that there should be no force on the pole, or if the sphere is at rest and the pole moving with velocity v there should be a force on the pole equal to $-ev/a^2$.

According to this we should expect a force on a unit magnetic pole, moving horizontally at the earth's surface, equal to ev/a^2 and in a horizontal direction perpendicular to the direction of motion of the pole. Thus, if a piece of iron is set moving in a horizontal direction at the earth's surface, we should expect forces on the atomic magnets in the iron the same as would be produced by a horizontal field of strength ev/a^2 in a direction perpendicular to the direction of motion.

An iron ring, about 100 cm. in diameter and 10 sq. cm. in cross-section, was wound with a uniform layer of insulated wire and mounted on a shaft along a diameter, so that it could be rotated rapidly with the shaft either

vertical or horizontal. The ends of the winding were connected, through a commutator and brushes, to a galvanometer. The galvanometer always indicated a considerable current, which appeared to be due to slight irregularities in the earth's magnetic field, and it was not possible to obtain satisfactory results with this apparatus.

A similar but much smaller apparatus was therefore constructed, which was completely enclosed in a double-walled iron case to screen off the earth's field. This apparatus also gave a current which was about the same with the axis of rotation, either vertical or horizontal. The current appeared to be due to residual magnetism in the iron case, which could not be got rid of.

A third and simpler apparatus was then set up and proved successful. This apparatus is shown diagrammatically in fig. 1. An iron bar AB, about

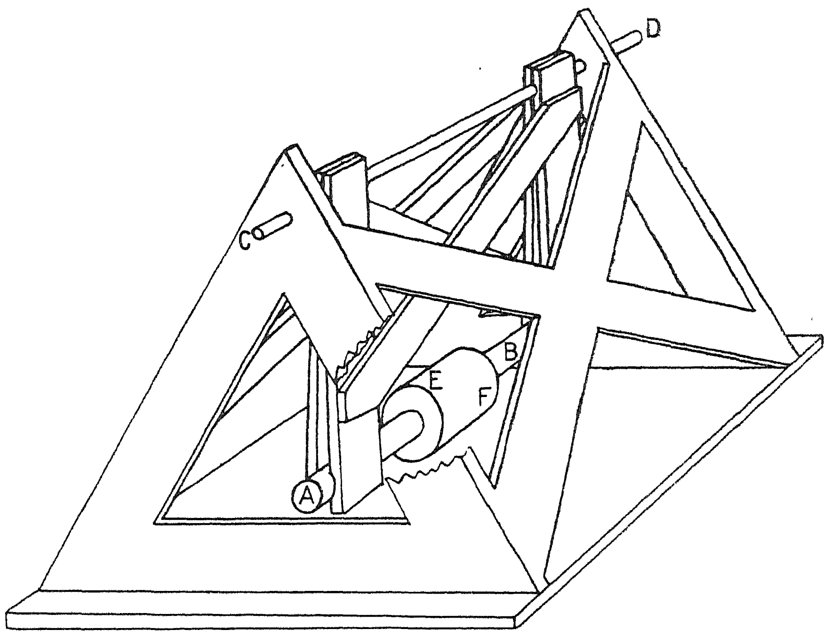


Fig. 1.

200 cm. long and 6 cm. in diameter, was suspended horizontally by means of a rigid wooden framework from a horizontal steel shaft CD, about 260 cm. long. The shaft was supported by bearings mounted on a rigid wooden frame on a table.

The bar AB when pulled to one side and let go could swing like a pendulum about CD as axis. Round the middle of the bar AB, a coil EF, of about 2,000 turns of insulated wire, was fixed. This coil was connected with a

sensitive fluxmeter by means of flexible leads. The bar AB was adjusted accurately parallel to the shaft CD, and the apparatus was very rigidly constructed, so that when the bar was swinging it moved exactly parallel to itself.

When the bar was set swinging the fluxmeter usually indicated a small alternating current. By placing a small magnet in a suitable position near the apparatus it was found possible to completely get rid of this current, so that the bar could be kept swinging without affecting the fluxmeter. There was then no deflection of the fluxmeter when the bar was moved very slowly from one extreme position to the opposite one, or when it was held fixed in any one position and then moved quickly to any other position and held there.

The magnetic induction along the bar was therefore then the same in any position to which it could swing, and was not changed appreciably when the bar was moving parallel to itself. These experiments were done with the bar pointing east and west, north and south, and in other positions.

The sensibility of the apparatus was measured by placing a bar magnet of known moment at a measured distance from the bar AB and parallel to it. The direction of the magnet was then reversed and the resulting deflection of the fluxmeter measured.

It was found that reversing a magnet, having a moment of 800 at a distance of 200 cm., gave a flection of 5 mm., which is therefore the deflection due to reversing a field of 10^{-4} Gauss along the bar. Approximately the same value of the sensibility was also obtained by calculation from the dimensions of the apparatus and the sensibility of the fluxmeter.

The effect to be expected is that due to reversing a magnetic field of strength ev/a^2, where v is the maximum velocity of the bar when swinging. The time of one oscillation was $1 \cdot 5$ secs. and the amplitude 25 cm., so that v was about 100 cm. per sec. Also $\rho = 5 \times 10^{-14}$ and $a = 6 \times 10^8$ so that

$$\frac{cv}{a^2} = \tfrac{4}{3} \pi \rho v a = 10^{-2} \text{ Gauss.}$$

Since reversing 10^{-4} Gauss gave 5 mm., reversing 10^{-2} Gauss would have given 500 mm. The observed effect was not more than $0 \cdot 1$ mm., so that the effect was less than one part in 5,000 of that calculated.

We conclude therefore that, if moving matter produces a magnetic field like that due to a moving charge of electricity, then the mass equivalent to one electrostatic unit is not less than 5,000 gravitational units, or 20,000 kilograms. If then the earth's magnetic field is to be explained by a slight modification of the laws of electrodynamics, the modification must be such

as to make rotating matter produce a magnetic field, but matter having a velocity of pure translation give no appreciable field.

If rotation, but not translation, of matter gives a magnetic field, then we should expect the moment of a rotating sphere to be proportional to the volume, so that the field at the equator would be independent of the radius for spheres of the same density and angular velocity.* But it is known that there is no appreciable field due to the rotation of small non-magnetic bodies, so that it seems probable that the earth's field cannot be due to an effect depending on angular velocity only.

The Secondary Corpuscular Rays produced by Homogeneous X-rays.

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(Communicated by Prof. Sir E. Rutherford, F.R.S. Received August 27, 1923.)

CONTENTS.

Introduction.

In the summer of 1914 I began, with the assistance of Mr. W. F. Rawlinson, an investigation of the velocities of the secondary cathode particles ejected from metallic surfaces by X-rays of known frequency. The source of X-rays then available was not very powerful, and little progress had been made when the work was interrupted by the war. A preliminary account of the experimental method, and of the few results which had been obtained, was communicated to the 'Philosophical Magazine,' and published in August, 1914.†

* Sir A. Schuster, 'Proc. Lond. Phys. Soc.,' p. 121 (1912).

† 'Phil. Mag.,' vol. 28, p. 277 (1914).

Briefly, the method consisted in exposing a narrow strip of metal* to the beam of X-rays, and using a uniform magnetic field to bend the stream of ejected electrons onto a photographic plate, the experiment being performed in a high vacuum. The product rH, where H is the strength of the magnetic field and r the radius of curvature of the path of an electron moving normally to the field, is characteristic of that electron: from it the kinetic energy of the electron may readily be calculated.

A special focussing device was used, and described in the paper referred to, by means of which quite a wide beam of electrons could be employed without impairing the definition of the resulting image on the photographic plate: this device not only appreciably shortens the exposures required, but also enhances the effect of the rays under investigation, relatively to that of the general scattered radiations. These latter are always troublesome, and cannot be entirely eliminated.

It is to be expected that homogeneous X-rays, of frequency ν, falling on the target will bring about the expulsion of electrons with kinetic energy $h\nu$—W, W being the work done in freeing an electron from its atom, and h Planck's constant. According to the theory of X-radiation which has been based on the Rutherford-Bohr atom-model, W may have any one of a number of discrete values characteristic of the material of the target; these permissible values of W are the values of the (negative) energy associated with the different quantised orbits within the atoms of the target. Numerically they will be given by $h\nu_K$, $h\nu_{L_I}$, $h\nu_{L_{II}}$ . . . $h\nu_{M_I}$ . . . , where ν_K, ν_{L_I} . . . are the critical X-ray absorption frequencies of the material of the target.

Thus, primary X-radiation, of a sufficiently high single frequency ν, should give rise to what may be called a "line spectrum" of secondary corpuscular rays from the target, this line spectrum being composed of groups of electrons from the different levels in the atom.

The ejection of these electrons is necessarily followed by the emission of the "characteristic" (fluorescent) X-radiation of the target. Each of the strong lines of the fluorescent spectrum produces in its turn a line spectrum of electrons from the more superficial levels of the atom, and so a very large number of lines may be expected in the complete corpuscular spectrum.

Some evidence of the phenomena indicated above was obtained in our experiments of 1914, but as at that time there was no detailed quantitative theory of X-ray line spectra, the very meagre experimental data we obtained could not be satisfactorily interpreted.

* Hereinafter referred to, for the sake of brevity, as the "target."

Since 1914 the same method has been used by Kang Fu Hu,* de Broglie,† and Whiddington.‡ De Broglie first succeeded in obtaining and interpreting line spectra of the type indicated by the theory, and his results were confirmed and extended by Whiddington. The accuracy claimed in these experiments was not, however, of a very high order—de Broglie estimates his magnetic fields as correct to 1 per cent., while Whiddington claims an accuracy of $\frac{1}{2}$ per cent. in his measurements of rH for the stronger lines, and these percentage errors are practically doubled in calculating the corresponding energies. Moreover, in each case the deviations of the experimental results from the values calculated from X-ray data are frequently much in excess of the estimated errors of experiment.

As an accurate knowledge of the energies associated with the different electronic orbits within the atoms is essential to the further development of the theory of atomic structure, it seemed well worth while to proceed with this work, refining the experimental methods wherever possible, and aiming at an accuracy not inferior to one part in 1,000 in the measurement of rH. In this connection it may be pointed out that the majority of the tabulated values of the energies of the different levels§ have been deduced indirectly from the X-ray emission spectra. Only a minority have been obtained by direct measurement of absorption spectra, and the experimental difficulties in the way of extending spectrographic methods to the long-wave limits are well known, *e.g.*, overlapping of spectra of different orders, and excessive absorbability of X-rays of corresponding wave-lengths, with additional complications due to regions of selective absorption by silver and bromine, if photographic registration is employed.

The K limits have been measured directly for most elements from uranium (92) to magnesium (12), the L limits from uranium to silver (47), and the M limits for three elements only—uranium, thorium (90) and bismuth (83); only in the cases of uranium and thorium have all five M limits been observed. The other X-ray spectral terms have been obtained by ascribing definite origins to the lines of the emission spectra, and applying the principle of combination to the available emission and absorption data—data which are not in all cases entirely consistent among themselves. Also, there are many cases in which this method of calculating the terms cannot be applied: for instance, there

* 'Physical Review,' vol. 11, p. 505 (1918).

† 'Comptes Rendus,' 1921 and 1922; 'J. de Physique,' September, 1921.

‡ 'Phil. Mag.,' vol. 43, p. 1116, 1922.

§ *E.g.*, Sommerfeld, 'Atombau,' 3rd Edn., p. 630; Bohr and Coster, 'Zs. Physik,' vol. 12, p. 342 (1923).

are no data from which the L_I levels of the lighter elements can be calculated, as there are no appropriate known terms and lines for combination; there is, of course, no line in the emission spectra corresponding to the transition $L_I - K$.

There is, therefore, an obvious need for direct measurements of these levels, and in many respects the study of the corpuscular spectra excited by X-rays of suitable frequency is specially adapted to this purpose, and is not beset by the same difficulties or subject to the same limitations as the spectrographic method. It also furnishes semi-quantitative information on the relative probabilities of extraction of electrons from the different orbits by X-rays of given frequency. At the same time, it must be admitted that it is very difficult to approach an order of accuracy equal to that attained under suitable conditions by the X-ray spectrometer. As the experiments to be discussed here represent an attempt at precision measurements on the corpuscular spectra, the apparatus and methods will be described in some detail.

Experimental Details.

(*a*) *Source of X-rays.*—It is highly desirable that the primary X-ray beam shall be at least approximately homogeneous: if it contains an appreciable amount of "white" radiation, it will obviously produce a continuous corpuscular spectrum; in addition, selective absorption by the target will lead to the production of relatively intense fluorescent radiation, of which the effect may mask the direct effect of the primary beam. This is very noticeable in the results of de Broglie and Whiddington, where most of the lines observed in the corpuscular spectra are due to the fluorescent X-rays of the target. As it is impossible to distinguish, for instance, between an electron expelled by the $K\alpha_1$ rays of the target from an L_{II} ring,* and one expelled by the $K\alpha_2$ rays from an L_{III} ring, it is evident that this part of the corpuscular spectrum cannot be exactly interpreted; it is well, therefore, to suppress it as far as possible, in the interests of the more certain identification and the more exact measurement of the spectrum excited directly by the primary X-rays.

Unfortunately the obvious method of isolating some strong X-ray line by reflexion from a crystal is not practicable in these experiments, because of the smallness of the intensity obtainable in this way. In most of the present series of experiments the copper K-rays were used. The copper anticathode, if the

* I use throughout the notation recently introduced by Bohr and Coster, in which the symbols K, L_I, L_{II}, L_{III}, M_I, . . . M_V, . . . stand for the different levels in diminishing order of strength of binding of the corresponding electrons.

tube is run at a suitable potential difference, gives much less general radiation than elements of higher atomic number. The rays were filtered by nickel foil, 0·015–0·025 mm. thick—sufficient to cut out the $K\beta$ rays almost completely: photographs of the filtered beam, taken by Seemann's method of reflexion from a calcite crystal, showed no trace of the $K\beta$ doublet, even when the $K\alpha$ doublet was considerably over-exposed.*

For the purpose of these experiments the filtered beam may be taken as consisting solely of the copper $K\alpha_1$ rays. The lines $K\alpha_1$ and $K\alpha_2$ would not be resolved, and the weaker and softer component $K\alpha_2$ would merely produce a slight broadening of the lines of the corpuscular spectrum on their low velocity sides. As it is a feature of the focussing method used that the measurements are made on the high velocity edges of the lines, this effect of the complexity of the primary X-ray beam does not come into consideration at all.

A number of experiments were also made, using the K-rays of silver, with a palladium filter; here, however, the filtration did not appear to be so complete, and the separation of the two $K\alpha$ lines was appreciable, so this series was abandoned.†

The X-ray tube used was of the type developed by Dr. A. Müller‡—small "gas-filled" glass and metal tube, with water-cooled anticathode. The anticathode could be placed within one or two centimetres of the target, thus allowing a fairly large proportion of the total output to be utilised. The X-rays emerge through a thin aluminium window (about 0·02 mm. thick), placed immediately in front of the anticathode. The tube was exhausted by a rotary Gaede mercury pump, and in normal running a few turns of the pump every two or three minutes sufficed to maintain the X-ray vacuum, in spite of the multiplicity of waxed joints which is characteristic of this type of tube. A liquid air trap was inserted between the pump and the X-ray tube to keep out mercury vapour from the latter. The current through the tube was derived from a high-tension transformer, and rectified by a thermionic valve.

(*b*) *Magnetic Field.*—In the final arrangement the magnetic field was produced by a pair of coils of the Helmholtz—Gaugain type. Each coil

* The nickel filter was also of service in cutting out the K-rays of zinc, which were emitted by some of the brass portions of the X-ray tube.

† Ledrus has also published a short account of experiments made with filtered silver K-radiation, which appeared while the present work was in progress ('C.R.,' vol. 176, p. 383, 1923).

‡ 'Phil. Mag.,' vol. 42, p. 419 (1921). I have pleasure in acknowledging Dr. Müller's valuable advice and assistance on matters connected with the running of this tube.

contained 528 turns of No. 18 S.W.G. copper wire, with a mean diameter of 39·6 cm., and the combination gave a field at the centre of very nearly 24 gauss per ampère of exciting current. The current passing through the coils was measured in the usual way, by comparing the drop of potential down a standard resistance with the E.M.F. of a standard cell.

It can readily be shown that with coils of these dimensions the magnetic field is constant to within one part in 1,000 up to nearly 5 cm. from the axis, and to one part in 400 up to 6 cm., and the variation can easily be allowed for.*

The X-ray tube was placed within the coils, with its axis nearly parallel to their common axis—*i.e.*, nearly parallel to the magnetic field: this minimises the disturbing effect of the field on the focussing of the primary cathode beam. The general arrangement is shown in plan in fig. 1, where X is the X-ray

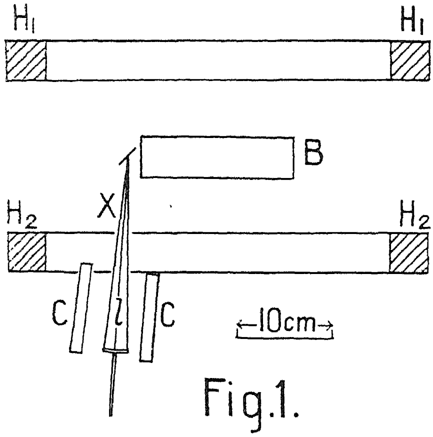


Fig. 1.

tube, and H_1, H_2 the coils. CC are small compensating coils, run in series with the main coils: the positions of CC are adjusted by trial, with the field on, until the maximum X-ray emission is obtained.† With this disposition of the apparatus, the stray field of the compensating coils, in the region utilised for the secondary cathode-ray measurements, is very small: in the experiments

* *Vide* Maxwell, 'Electricity and Magnetism,' or A. Gray, 'Absolute Measurements.'

† It is not essential that the compensating coils should exactly neutralise the magnetic field at all points on the path of the cathode stream: all that is required is that $\int_0^l (l-x)\,\mathrm{F}dx$ should be approximately zero, where l is the distance cathode—anti-cathode, x is measured along the axis of the tube, and F is the component of magnetic force perpendicular to the axis. The integral does not contain the velocity of the cathode rays, so the compensation, once made, is independent of the hardness of the tube.

it was of the same order of magnitude as the earth's field, and was measured with a vibration magnetometer, while coils H_1, H_2 were short-circuited.

B, in the figure, is the "camera"—an evacuated metal box—containing the focussing arrangement and the photographic plate.

(*c*) *Focussing Apparatus.*—The focussing device used in most of the experiments differed slightly from that used in the previous work, in that a wide target and narrow slit were used instead of a narrow target and wide slit, the principle, however, being the same.* The arrangement is represented in fig. 2. T represents the target, S the slit, and PP the photographic plate.

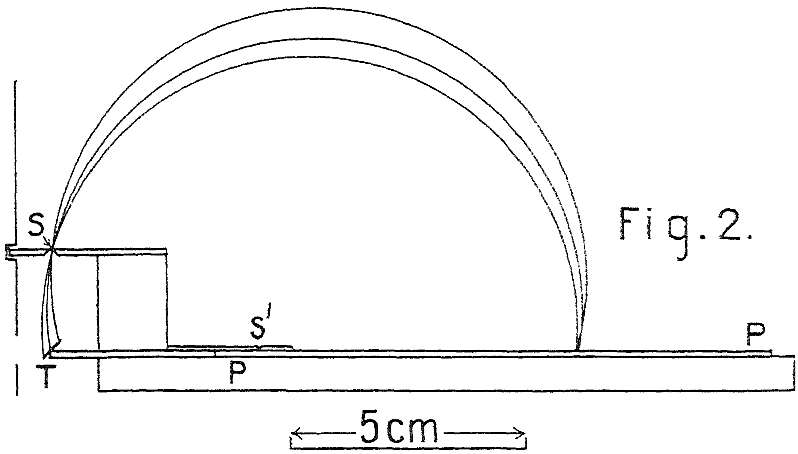


Fig. 2.

S^1 is a fine slit by means of which a fiducial mark is made on the plate. An important advantage of this arrangement is that the *exact* position of the target is immaterial; so long as it is placed with its centre *approximately* on the prolongation of the photographic plate, and vertically below the slit, homogeneous secondary cathode rays from it are focussed in a sharp line on the plate. The quantities entering into the calculation of the radius of curvature corresponding to any line on the plate are then the vertical height of the slit above the surface of the plate, and the horizontal distance between the slit and the high-velocity edge of the line. Thus the important constants of the apparatus are the relative positions of the two slits, S and S^1, which can be determined with great accuracy with a travelling microscope, and which are not affected by interchanging different targets. It is therefore not necessary to measure up the apparatus every time the target is changed, and

* This modification was first tried by Ellis in his work on the secondary β rays produced by γ rays.

the values of r corresponding to all positions of the lines may be tabulated once for all.

The target was a strip about 4 mm. wide and 15 mm. long. It was made as thin as possible—*e.g.*, metal leaf when available, as in the cases of gold, silver, etc., in other cases thin layers of suitable salts of the element under investigation—and supported by a strip of thin aluminium. From the point of view of the expelled corpuscular radiation, there is no advantage in having the target more than about a hundred molecules thick, as cathode rays of the velocities dealt with are very rapidly absorbed and "straggled" by matter, and only those from the surface layers emerge with their full velocity. Any increase in the thickness of the target only serves to increase the relative effect of the fluorescent X-rays.

The focussing apparatus was enclosed in a brass box, closed air-tight by a greased brass plate. The box was lined with aluminium, and suitable screens were inserted to cut down scattered radiations from the walls. The X-rays entered the box through a window of thin aluminium or nickel foil. The box was exhausted first by the Gaede pump, then by charcoal in liquid air, the charcoal tube being connected with the box by short, wide tubing with no stopcock or other obstruction. No direct measurements were made of the pressure, but the box could be put into communication with the X-ray tube by opening a stopcock; during any experiment, opening this stopcock for a few seconds hardened the tube to such an extent that it was impossible to maintain the discharge through it. As the charcoal tube was on the side of the box remote from the X-ray tube, it could reasonably be assumed that the vacuum in the camera was very high. This point is of great importance when dealing with cathode rays of low velocity.

(*d*) *Photographic Plates.*—Many varieties were tried, ranging from extra rapid to very slow "Process" plates, but Ilford X-ray plates were found to give the best results in most cases: with the slowest rays measured (RH about 140 Gauss cm.) rather better results were obtained with Paget "Half-tone" plates, which have a much thinner sensitive film.

Calculation of results:—

The energies of the expelled cathode particles were calculated from the formula

$$mv/e = r\mathrm{H},$$

where m = mass of electron, v = velocity, and e = charge in E.M.U.

Then if $\beta = v/c$, where c is the velocity of light,

$$\beta^2 = \frac{(mv/e)^2 \times (e/m_0)^2}{c^2 + (mv/e)^2 (e/m_0)^2}$$

and energy $= m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right)$

For convenience in comparing with the published tables of X-ray data, the energies were expressed in terms of the equivalent ν/R*—*i.e.*,

$$\frac{\text{energy}}{h \times \text{Rydberg frequency}}.$$

The following values were adopted for the constants involved in the formulæ :—

$$e/m_0 = 1 \cdot 7686 \times 10^7 \text{ E.M.U./gramme.}$$

$$e = \frac{4 \cdot 774 \times 10^{-10}}{c} \text{ E.M.U.}$$

$$h = 6 \cdot 545 \times 10^{-27} \text{ erg. sec.}$$

$$R = 109737 \times c, \quad c = 3 \times 10^{10} \text{ cm./sec.}$$

and the value of ν/R for the $K\alpha_1$ line of copper was taken as $592 \cdot 8$.

The relativity correction, which is negligible for low velocities, amounts to $0 \cdot 8$ per cent. of the total energy for a cathode ray with $r\text{H} = 300$ Gauss cm., so has to be taken into account. As the calculation of the energies corresponding to a large number of spectral lines is rather tedious, a table was prepared, giving $\log (\nu/R)$ against $\log r\text{H}$ at suitable intervals. As $\dfrac{d \log \frac{\nu}{R}}{d \log r\text{H}}$ varies quite slowly—from 2 for very small values of $r\text{H}$ to $1 \cdot 984$ for $r\text{H} = 300$, and $1 \cdot 957$ for $r\text{H} = 500$—a relatively short table suffices for the computation of intermediate values with sufficient accuracy by interpolation of the logarithms, and the arithmetical labour is considerably reduced.

The results which have been obtained with the copper $K\alpha_1$ rays are tabulated below.

* 1 unit = $13 \cdot 54$ "equivalent volts."

Results.

83. Bismuth (Bi_2O_3).

Remarks.	Intensity.	rH	ν/R	$592 \cdot 8 - \nu/R$	Origin.	Bohr and Coster's ν/R† Bismuth.
	1	213·4	296·3	296·5	M_I	$M_I = 295 \cdot 9$
	2	221·9	320·3	272·5	M_{II}	$M_{II} = 273 \cdot 6$
	5	234·6	357·6	235·2	M_{III}	$M_{III} = 234 \cdot 0$
	6	245·8	392·5	200·3	M_{IV}	$M_{IV} = 199 \cdot 4$
	6	248·5	401·2	191·6	M_V	$M_V = 191 \cdot 4$
	2	283·6	521·5	71·3	N_I.	$N_I = 71 \cdot 0$
	3	286·4	531·8	61·0	N_{II}	$N_{II} = 58 \cdot 7$
	4	289·1	541·8	51·0	N_{III}	$N_{III} = 50 \cdot 3$
Not resolved, approximate value	4	292·5	554·6	38·2	N_{IV}	$N_{IV} = 35 \cdot 7$
	5	293·8	559·5	33·3	N_V	$N_V = 33 \cdot 7$
Broad band, diffuse	3–4	300·2*	584·0	8·8	N_{VI}, N_{VII}, O	$N_{VI} = 13 \cdot 6$; $N_{VII} = 13 \cdot 0$; $O = 11-2$

* Approximate position of head of band—very difficult to measure accurately, as band tails off on high-velocity edge.

† As a result of more recent precision measurements of the low-frequency X-ray lines, E. Hjalmar gives the following values :—

N_I, 69·1 ; N_{II}, 61·3 ; N_{III}, 51·2 ; N_{IV}, 34·8 ; N_V, 32·1 ; N_{VI}, 13·3 ; N_{VII}, 13·0 ; $O_{\overline{II}}$, 10·2 ('Zs. Physik.,' vol. 15, p. 65, 1923).

82. Lead (metal).

Remarks.	Intensity.	rH	ν/R	$592 \cdot 8 - \nu/R$	Origin.	Bohr and Coster's ν/R* Lead.
	1	217·8	308·5	284·3	M_I	$M_I = 283 \cdot 8$
	1	225·2	329·8	263·0	M_{II}	$M_{II} = 262 \cdot 3$
	5	237·2	365·7	227·1	M_{III}	$M_{III} = 226 \cdot 0$
	5	248·6	401·7	191·1	M_{IV}	$M_{IV} = 190 \cdot 5$
	6	251·3	410·2	182·6	M_V	$M_V = 183 \cdot 0$
Head of band	4*	289·6	543·8	49·0	N_I–N_{III}	$N_I = 66 \cdot 0$; $N_{III} = 49 \cdot 3$
	6	294·3	561·4	31·4	N_{IV}, N_V	$N_{IV} = 32 \cdot 2$; $N_V = 30 \cdot 5$
	4	300·4	584·6	8·2	N_{VI}, N_{VII}, O	$N_{VII} = 10 \cdot 3$; $O_{III} = 6 \cdot 4$

* Hjalmar (*loc. cit.*) gives : N_I, 65·8 ; N_{III}, 47·4 ; N_{IV}, 31·3 ; N_V, 30·7 ; N_{VI}, 10·6 ; N_{VII}, 10·2 ; O_{II}, 8·0.

79. Gold (metal).

Remarks.	Intensity.	rH	ν/R	$592\cdot8 - \nu/R$	Origin.	Bohr and Coster's ν/R* Gold.
	1	228·4	339·2	253·6	M_I	$M_I = 252\cdot9$
	2	235·3	359·9	232·9	M_{II}	$M_{II} = 235\cdot1$
	5	245·2	390·6	202·2	M_{III}	$M_{III} = 202\cdot8$
	6	255·8	424·9	167·9	M_{IV}	$M_{IV} = 169\cdot3$
	6	257·7	431·3	161·5	M_V	$M_V = 163\cdot0$
Foot of band, approximate position	4	288·2	538·6	54·2 } band	N_I–N_{III}	$N_I = 58\cdot0$
Head of band	5	292·4	554·2	38·6 } band	N_I–N_{III}	$N_{III} = 42\cdot8$
	5	296·6	570·2	22·6	N_{IV}, N_V	$N_{IV} = 26\cdot4$; $N_V = 25\cdot0$
	3	302·0	591·0	1·8	N_{VI}, N_{VII}, O	6·4 — 0·8

* Hjalmar (*loc. cit.*)—N_I, 57·3 ; N_{III}, 37·5 ; N_V, 25·2 ; N_{VI}, 7·1 ; N_{VII}, 6·7.

74. Tungsten (metal and WO_2).

Remarks.	Intensity.	rH	ν/R	$592\cdot8—\nu/R$	Origin.	Bohr and Coster's ν/R Tungsten.
	2	243·2	384·3	208·5	M_I	$M_I = 207\cdot6$
	2	249·2	403·4	189·4	M_{II}	$M_{II} = 188\cdot9$
	5	255·9	425·3	167·5	M_{III}	$M_{III} = 167\cdot4$
Not resolved, approximate	6	264·4	453·8	139·0	M_{IV}	$M_{IV} = 137\cdot8$
	6	266·1	459·6	133·2	M_V	$M_V = 133\cdot2$
Head of band	4	294·3	561·4	31·4	N_I–N_{III}	$N_I = 43\cdot6$; $N_{III} = 30\cdot6$
	5	298·0	575·6	17·2	N_{IV}–N_V	$N_{IV} = 18\cdot7$; $N_V = 17\cdot8$
	3	302·6	593·3	— 0·5	N_{VI}–N_{VII}–O	5·2 — 0

56. Barium ($BaCO_3$).

Remarks.	Intensity.	rH	ν/R	$592 \cdot 8-\nu/R$	Origin.	Bohr and Coster's ν/R Barium.
	1	151·4	149·5	443·3	L_I	$L_I = 442 \cdot 3$
	1	165·6	178·7	414·1	L_{II}	$L_{II} = 414 \cdot 7$
	6	178·2	206·8	386·0	L_{III}	$L_{III} = 386 \cdot 7$
Diffuse	5	202·4	266·7	—	Fluorescent L—M	—
Diffuse	3	221·7	319·7	—	Fluorescent L—M	—
Head of band (?)	4	276·8	497·0	95·8	M_I	$M_I = 95 \cdot 4$
	6	279·8	507·9	84·9	M_{II}	$M_{II} = 84 \cdot 9$
	6	281·5	513·8	79·0	M_{III}	$M_{III} = 79 \cdot 4$
	5	287·1	534·4	58·4	M_{IV_1} M_V	$M_{IV} = 58 \cdot 8$, $M_V = 58 \cdot 7$
	3	291·5	551·0	41·8	K oxygen?*	
	3	293·9	559·8	33·0	K carbon?*	
Head of band	4	298·9	578·9	13·9	N_I–N_{III}	$N_I = 18 \cdot 8$, $N_{III} = 14 \cdot 4$
	2	302·6	593·2	— 0·4	N_{IV}—O	7·1—2·1

* For K oxygen, Foote and Mohler give 35·3; Kurth, 38·3.
For K carbon, Foote and Mohler give 20·0; Kurth, 21·4.

53. Iodine (LiI and AgI).

Remarks.	Intensity.	rH	ν/R	$592 \cdot 8-\nu/R$	Origin.	Bohr and Coster's ν/R Iodine.
	2	179·4	209·7	383·1	L_I	$L_1 = 382 \cdot 6$
	3	190·5	236·2	356·6	L_{II}	$L_{II} = 357 \cdot 6$
	6	198·2	255·6	337·2	L_{III}	$L_{III} = 336 \cdot 0$
	5	281·2	512·8	80·0	M_I	—
	6	284·9	526·3	66·5	M_{II}-M_{III}	$M_{II} = 69 \cdot 0$, $M_{III} = 64 \cdot 8$
	5	290·2	546·2	46·6	M_{IV}-M_V	$M_{IV} = 46 \cdot 8$, $M_V = 46 \cdot 0$
Head of band	4	300·1	583·6	9·2	N, O	—

50. Tin (metal).

Remarks.	Intensity.	rH	ν/R	592·8—ν/R	Origin.	Bohr and Coster's ν/R* Tin.
	2	201·0	263·0	329·8	L_I	L_I =328·7
	3	209·3	285·0	307·8	L_{II}	L_{II} =305·6
	5	215·5	302·1	290·7	L_{III}	L_{III} =289·4
Head of a narrow band(?)	4	285·2	527·5	65·3	M_I	M_I = 65·1
Narrow band	5	288·6	540·1	52·7	M_{II}, M_{III}	M_{III} = 52·4
Narrow band	3	293·2	557·3	35·5	M_{IV} M_V	M_V = 35·8
Diffuse, broad band	2	300·5	585·2	7·6	N	—

* Not given by Bohr and Coster: above values are interpolated from Bohr and Coster's $\sqrt{(\nu/R)}$ values.

47. Silver (metal and AgI).

Remarks.	Intensity.	rH	ν/R	592·8—ν/R	Origin.	Bohr and Coster's ν/R Silver.
	3–4	219·3	312·8	280·0	L_I	L_I =279·5
	4	226·2	232·7	260·1	L_{II}	L_{II} =260·0
	5	230·9	346·6	246·2	L_{III}	L_{III} =247·3
Head of a band, not quite resolved.	5	289·9	544·9	47·1	M_I, M_{II}	M_I = 53·3; M_{II} = 43·5
	6	292·2	553·5	39·3	M_{III}	M_{III} = 41·2
	2	296·3	569·0	23·8	M_{IV}–M_V	M_V = 27·5
Head of band	3	302·0	591·0	1·8	N	N=7·5–0·6

42. Molybdenum (metal).

Remarks.	Intensity.	rH	ν/R	592·8—ν/R	Origin.	Bohr and Coster's ν/R Molybdenum.
	3	242·1	380·7	212·1	L_I	L_I =211·9
	4	248·0	399·4	193·4	L_{II}	L_{II} =193·9
	5	250·2	406·7	186·1	L_{III}	L_{III} =186·2
	3	295·1	564·4	28·4	M_{III}(?)	M_{III} = 29·7
Approximate values	2	297·7	574·5	18·3	M_V (?)	M_V = 17·2
	1	301·7	589.7	3·1	N (?)	M_{III} = 3·0

38. Strontium ($SrCO_3$).

Remarks.	Intensity.	rH	ν/R	$592\cdot8-\nu/R$	Origin.	Bohr and Coster's ν/R* Strontium.
	5	256·6	427·6	165·2	L_I	L_I = 162·0
Not quite resolved: approximate.	5	261·2	443·0	149·8	L_{II}	L_{II} = 147·0
	5	262·4	447·0	145·8	L_{III}	L_{III} = 142·5
Diffuse bands, not accurate.	2	291·7	551·6	41·2	Oxygen K(?)	—
	3	296·2	568·6	24·2	M (?)	—
	1	302·4	592·5	0·3	N (?)	—

* Not given by Bohr and Coster: extrapolated from nearest $\sqrt{(\nu/R)}$ values.

29. Copper (metal).

Remarks.	Intensity.	rH	ν/R	$592\cdot8-\nu/R$	Origin.	Bohr and Coster's ν/R Copper.
	5–6*	280·6	510·8	82·0	L_I	—
	5	284·0	523·1	69·7	L_{II}-L_{III}	L_{II} = 71·3; L_{III} = 69·8
Band tailing off in intensity on high-velocity side.	3–2	300·8	586·3	6·5	M	M_{II}-M_{III} = 5·2

* L_I just perceptibly more intense than L_{II}-L_{III}.

Light Atoms—Collected Results (Targets of $CaSO_4$, $CaCO_3$, K_2SO_4, MgO, Na_2SO_4).

Element.	rH	ν/R	$592\cdot8-\nu/R$.	Origin.	Other values.	Remarks.
20. Calcium	213·0	295·2	297·6	K	297·5 (1)	—
19. Potassium	224·1 (?) 296·3	326·6 569·0	266·2 23·8	K L* (?)	265·3 (1) L_{III} 21·2 (1)	— Faint, not accurate.
16. Sulphur	251·1 (?) 298·2	409·5 576·3	183·3 16·5	K L* (?)	181·8 (1) L_{III} = 11·8 (1)	— Faint, not accurate.
12. Magnesium	275·7 (?) 300·4	493·2 584·8	99·6 8·0	K L* (?)	95·8 (1) L_{III} = 3·5 (1)	— Faint.
11. Sodium	280·8	511·5	81·3	K	—	—
8. Oxygen	291·4	550·5	42·3	K	35·3 (2) 38·3 (3)	—

* L_I is probably more prominent than L_{III} in these regions.
(1) Bohr and Coster (Fricke's results for K levels).
(2) Foote and Mohler —*Cf.* Foote and Mohler, 'Origin of Spectra.'
(3) Kurth " " "

Discussion of Results.

The figures appearing in the column headed "Intensity" will be discussed later: the higher numbers characterise the stronger lines. In the last column are reproduced, for the purpose of comparison, the values of the energy-levels tabulated by Bohr and Coster. The numerical agreement will be seen to be in general extremely good—indeed, in some cases so good as to appear almost to call for an apology, especially when it is remembered that the above method of displaying the results in terms of energies [or $(r\mathrm{H})^2$] magnifies any errors of measurement. In any case the figure following the decimal point in the calculated values of ν/R cannot have much significance, though I have left the results exactly as they were first calculated, instead of rounding them off to the nearest unit or half-unit.

An example of the actual results obtained with two different fields is given below:—

Bismuth Target.

2 amps. (mean of two plates).		2·5 amps. (one plate: not very good photo.)	
Intensity.	rH	Intensity.	rH
1	213·3	1	213·8
2	221·8	2	222·1
6	234·5	5	234·7
6	248·4	6	248·7
broad band (?)	274·0	–	—
2	283·3	(band) 2	284·2
3	286·3	3	286·6
4	289·0	3	289·2
4	292·5	–	not resolved.
5	293·8	5	293·9
broad band diffuse 3–4	300·3	broad band 3–4	300·1

This represents the result of a single set of measurements on the three plates and is a very fair example of the type of agreement obtained: I have been careful not to select a particularly favourable specimen.

No line is included in the collected results unless it has been identified on several plates, and in many cases the lines have been measured in three or four different fields, covering widely different values of H. In addition to the lines tabulated, many of the plates (including the example given above) show a diffuse band, of intensity 1–2 on my scale, in the region $r\mathrm{H} = 270$–280 approximately: this was traced to the effect of electrons ejected from the K rings of the aluminium supports on which the target was fixed. Further,

some of the photographs taken with the stronger magnetic fields show a few weak lines corresponding to values of ν/R much greater than 592·8—*e.g.*, on some plates lines were measured up to $\nu/R = 830$. These were not measured with extreme accuracy, as they lie outside the range for which the apparatus was designed, but it was found that they could very well be accounted for as a result of the action of the stronger lines of the L spectrum of mercury. As it was very likely that there would be some slight contamination of the copper anticathode by mercury vapour from the pump (*Cf.*, Müller, *loc. cit.*), no further attention was paid to these lines.

Returning to the question of the accuracy of the tabulated results, the *absolute* value of the magnetic field is the most difficult factor to estimate accurately. The determination of "r" depends on what is practically a straightforward measurement of a length of about 10 cm.; these measurements were, I think, certainly accurate to within 1/20 mm., as shown by the agreement between plates taken under identical conditions. The general excellence of the agreement between plates taken with different fields indicated the absence of systematic errors, such as might be introduced by inaccurate measurement of the plate-holder. At the same time, this agreement inspires confidence in the accuracy of the measurements of the current in the coils—*i.e.*, in the *relative* values of the different magnetic fields employed. The corrections for the external field of the compensating coils, and for the effect of distance of the paths of the electrons from the axis of the Helmholtz coils, were small, and it would be impossible for an error greater than one part in 2,000 of the value of rH to be introduced in making these corrections. On the whole, I think one part in 1,000 is a fair estimate of the probable error in rH, though if all the errors go the same way it might be a little greater; in this connection, I must admit that the accuracy with which the lines could be measured considerably exceeded the most sanguine expectation, and in view of this the arrangements for producing the magnetic field might have been improved upon (the Helmholtz double coil is very convenient for this work, but is not easy to set up accurately, and, although this part of the work was done with great care, a slight lack of rigidity in the mounting may have introduced small errors).

The possible sources of error which cannot be controlled in these experiments are the values which have to be assumed for the frequency of the primary X radiation, and for the fundamental constants e, $\frac{e}{m_0}$, h and c. The first of these quantities, and the X-ray data tabulated by Bohr and Coster, depend upon

crystal measurements, and are presumably referred to the conventional lattice-constant (Moseley's value) of $2 \cdot 814 \times 10^{-8}$ cm. for rock-salt. In the calculation of this quantity e only appears to the one-third power, but there are other uncertain factors, and there appears still to be some difference of opinion among X-ray spectroscopists as to the absolute accuracy of the wave-length measurements. It seems likely that one part in 1,000 is a possible value of the error introduced in this way: the existing X-ray data do not always agree among themselves to anything approaching this order of accuracy, as may easily be shown by trying at random a few combinations from the tables.

On the whole, the general nature of the numerical agreement shown by the table of results is circumstantial evidence for the accuracy of the values adopted for the various constants, although in view of the involved way in which they occur in the calculations the possibility of mutual compensation of errors cannot be excluded.

It will be seen from the tables that the analysis of the corpuscular spectra can be carried far beyond the regions which have been dealt with by X-ray spectroscopy. Thus, the measurements of the L* absorption edges have been carried much further than heretofore: it is just possible with the apparatus in its present form to distinguish all three of these limits as far down as strontium (38): here the lines corresponding to L_{II} and L_{III} are approximately $0 \cdot 5$ mm. apart on the photographs. It will be obvious from the method of the experiments that if two lines are too close to be separated by the resolving power of the apparatus, only the one corresponding to the spectral term with the *lower* value of ν/R can be measured accurately—in the above case L_{III}. For elements lighter than strontium, only L_I and L_{III} can be measured.

Again, all five M rings can be identified with the greatest ease in the case of bismuth (83) where only three have previously been measured. I am not aware of any spectroscopic measurements of the M absorption edges of elements lighter than bismuth,† but in the present experiments all five can be easily observed even for tungsten (74), though M_{IV} and M_V are not clearly separated. M_I, M_{II}, M_{III}, and M_V, can be traced down as far as barium (56).

It will be seen also that in the case of bismuth even the N rings are clearly

* The discussion of the measurements of the K levels of the very light atoms (which have been carried down as far as oxygen) is reserved till the end of the paper.

† Ross has measured four critical potentials for the excitation of the M lines of lead (Summary in 'Phys. Rev.,' vol. 18, p. 336 (1921)).

2 L 2

displayed,* though these cannot be traced with any confidence very far down the series of the elements. The apparatus was not designed to give accurate results in these regions, and the numerical values obtained for these levels, which come out as the small differences between two large numbers, cannot be very exact. The photographs, however, provide a very convincing demonstration (if any were needed at this stage) of the accuracy of the picture of the emission processes which has been evolved by Kossel, Sommerfeld, Smekal, Wentzel, Bohr, Coster, Dauvillier and others in the task of systematising X-ray spectra.

Re-examination of some of the photographs suggests that it might be just possible in some cases to separate a few more lines corresponding to small values of ν/R, in addition to those which have been tabulated. In view of the necessarily approximate nature of such results (and the difficulty of avoiding a certain mental bias in re-reading the photographs after the prominent lines have been identified) I have not thought it worth while to strain the interpretation of the plates any further, and the spectra are given as they were first measured. I have, however, revised the estimates of the intensities of some of the lines on the earlier photographs. It is hoped in the near future to modify the apparatus and to carry out measurements in other regions of the spectra, using still softer primary rays.

In addition to its adaptability to different spectral regions, it may be pointed out that the method of "corpuscular spectrometry" has another advantage over the more direct method of measuring absorption edges: the electrons are given sufficient energy to tear them right away from their parent atoms, without any opportunity of settling down in unoccupied outer orbits. The lines are therefore quite sharp—there is no "fine structure" effect in the photographs.

There is one other point to be mentioned in connection with the table of results: Whiddington† states that if ν is the frequency of an X-radiation falling on a target, and ν_P the frequency corresponding to the binding of one of the types of electron in the target, no line corresponding to $\nu - \nu_P$ appears in the corpuscular spectrum unless $\nu > 2\ \nu_P$. As there is no obvious physical reason underlying such a restriction of the validity of the Einstein photoelectric equation, this statement is of considerable theoretical interest. The

* Sommerfeld has said ('Atombau,' 3rd Edition, p. 229) that the number (7) of N rings assumed for the purpose of explaining X-ray spectra "hat zunächst keine Aussicht, experimentell nachgewiesen zu werden"—referring, of course, to spectroscopic methods.

† *Loc. cit.*, p. 1126.

restriction does not, however, appear to hold in the regions examined in the present experiments—in fact, all the lines which should be excluded by this relation appear on the plates, without a single exception. Such lines are those corresponding to bismuth M_I, barium and iodine L_I, L_{II}, and L_{III}, tin L_I and L_{II}, and calcium K, and some of these are quite intense.

It seems just possible that Whiddington's results may be partly explicable by the assumption that a sufficiently high vacuum was not maintained in the camera during all these experiments: in that event, low-speed electrons, corresponding to small values of $\nu - \nu_P$, might be so scattered by the residual gas that they would not produce a recognisable line on the photographic plate. In Whiddington's experiments the camera appears to have been permanently connected with the X-ray tube, and as the latter was of the cold cathode type, there must have been an appreciable gas pressure; in my experience with rather slower cathode rays, good photographs were not obtained unless the camera was much more highly evacuated than the X-ray tube. It may be significant that no very slow electrons are in fact recorded among Whiddington's results; on the other hand, some of his missing lines would correspond to electrons faster than some which he has detected, so this explanation is not entirely satisfactory.

Relative Intensities of the Lines.

Some further discussion is needed of the "Intensities" of the lines (*vide* Column 2 of the tables). The number 6 is used to indicate a very strong line, and 1 the faintest line which can be measured with certainty. All lines of intensity 2 and upwards can be seen at once on the plates, without special illumination, and by "untrained" observers.* Lines of intensity 1 sometimes require special illumination, and a well-rested eye, before they can be seen. All such lines have, however, been measured on several plates, and generally in different magnetic fields, so there is no possible doubt of their reality.

No very strict quantitative sense can be attached to the actual numbers given in Column 2, as the intensity of a photographic image is controlled by so many factors, and visual estimates must in any case be somewhat arbitrary. The cathode rays dealt with had values of ν/R ranging between 150 and 600 approximately (2,000-8,000 "volts"). It seems probable that even the fastest of these would lose most of their energy in the very thick and rich emulsion of the plates used in most of the experiments, and so the faster rays would produce a proportionately greater photographic effect (in very marked

* *E.g.*, Visitors to the Laboratory.

contrast with what is observed in the case of the much faster β rays from radium B and C). This point was very roughly tested by comparing photographs taken under identical conditions with different kinds of photographic plates. The method of comparison was crude, and the effects not very marked, but it certainly appeared that the faster rays showed up relatively more intensely on the thicker plates.

The tabulated intensities refer to the effects produced in a thick plate, so contain a factor dependent on the energy of the rays as well as their number. There is a partial compensation of the effect of the energy of the rays, due to the geometry of the apparatus, which allows a greater proportion of the more deviable rays to be brought to a focus on the photographic plate. Taking this into account, if the intensities could be measured absolutely, they would represent very approximately the product (number of electrons of a group ejected $\times$ square root of the energy of each electron in the group). It is obvious that the estimated intensities are not absolute values, or even accurate relative values, but the above is an approximation to their meaning.

Some evidence of the reliability of the estimates was obtained by exposing two plates, one with a target of $CaSO_4$, the other with K_2SO_4. In the first case the calcium and sulphur K lines were estimated as of equal intensity; in the second, the potassium and sulphur lines were estimated as 6 and 4 respectively—in fair agreement with that would be expected from the numbers of each kind of atom in the target.

I have mentioned these points in some detail, because the question of the amounts of energy appearing in the different groups of secondary electrons is of great theoretical interest. Ellis,* from the results of his work on the excitation of β rays by hard γ rays, concluded that "the greater the energy of binding of an electron the greater is the probability of its absorbing this hard γ radiation." Thus there was much more secondary β ray emission from the K rings than from the L rings of the target (in spite of the almost certainly greater number of L electrons), and the contribution of the peripheral electrons was negligible. Whiddington† found the same general type of distribution of intensities in the X-ray region which he investigated, and concluded that his results were a confirmation of those of Ellis.

Ellis‡ also showed later that, in interpreting the "natural" β ray spectra of the radioactive elements, it was necessary in some cases to assume that the

* 'Roy. Soc. Proc.,' A, vol. 99, p. 261 (1921).

† *Loc. cit.*, p. 1125.

‡ 'Proc. Camb. Phil. Soc.,' vol. 21, p. 121 (1922).

electrons of the L_I* sub-group absorbed more hard γ radiation than those of the L_{II} or L_{III} sub-groups. At first sight this appears in striking contrast with the results of experiments in the normal X-ray regions—*i.e.*, the regions in which X-rays are most easily investigated by crystal reflexion methods, and in which therefore the data are most complete. For instance, in the measurements of the L-absorption edges of the heavier elements, the L_{III} edge is by far the most, and L_I the least, prominent. This does not, however, conflict with Ellis's results, as the conditions in the two types of experiment are entirely different: in the measurement of absorption edges the electrons concerned are lifted out of their orbits by X-rays possessing just the requisite frequency, while the γ rays have frequencies many times greater than this. On the other hand the conditions controlling the effects observed in the regions of selective absorption seem also to operate over a fairly wide range. This is shown by the distribution of intensity in the characteristic X-ray emission spectra; in general, in the L spectra, most of the energy appears in the lines which correspond to electrons returning to the L_{III} ring; next in total energy is the L_{II} sub-group of lines, and last the L_I sub-group (using Sommerfeld's† approximate average values of the intensities of the lines, the ratios of the total energies in the three sub-groups are $L_{III} : L_{II} : L_I :: 23 : 13 : 8$). This must mean that under ordinary conditions of X-ray excitation the L_{III} electrons are much more frequently expelled than the L_{II} or L_I. How far this is simply due to the relative numbers of electrons in the different sub-groups is an open question; it appears certain, however, that to some extent it depends upon some intrinsic property of the corresponding electronic orbits—or, more precisely, to some relation between the orbits and the mechanism causing the ejection.

It may be pointed out here that the conditions under which the emission spectra have been observed have not been very widely varied; at all events, I am not aware that any attention has been drawn to marked variations in the relative intensities of the principal emission lines of a series under different conditions of excitation.‡ Most of the experiments have naturally been made with the conditions adjusted either for maximum output or for avoidance of overlapping of spectra; in the case of excitation by fluorescence, either

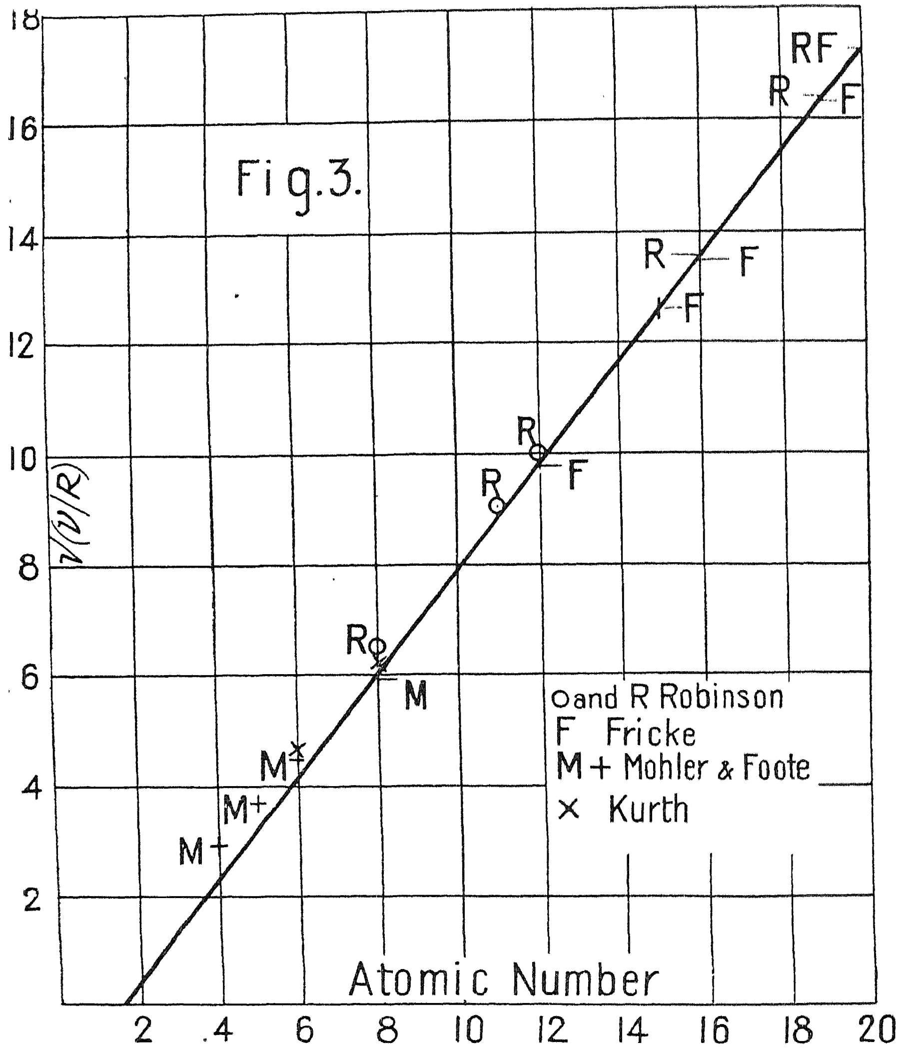
* Usually known as L_3: the old notation used by de Broglie and other pioneers in this field is naturaly more familiar in this connection, so perhaps it may be advisable to repeat that I am using the revised notation, in which the order of the suffixes is inverted.

† 'Atombau,' 3rd Edn., p. 196.

‡ Leaving, of course, out of consideration such experiments as those of D. L. Webster and others, which deal only with small ranges in the neighbourhood of the critical excitation potentials.

"white" radiation or radiation just harder than that to be excited have been used.

Now consider the data given in the "Intensity" column of the table of results. Here the exciting radiation in all cases is of "frequency" (ν/R) 592·8.



In the case of the L levels it is found that for the heavier elements the level L_{III} is the most effective in the emission of the secondary electrons, and L_{I} the least effective, in agreement with the deductions from X-ray data. This holds from barium to molybdenum, the range of ν/R values being from 443 to 186. With decreasing strength of binding—*i.e.*, going down the list of the

elements—the differences between the effects of the different rings become appreciably less pronounced. In the case of strontium (ν/R 146–165) the three L lines are of approximately equal intensity, and with copper (ν/R 70–82) L_I is just perceptibly the strongest line—in spite of the fact that L_{II} and L_{III} are so close that they are measured as a single line.

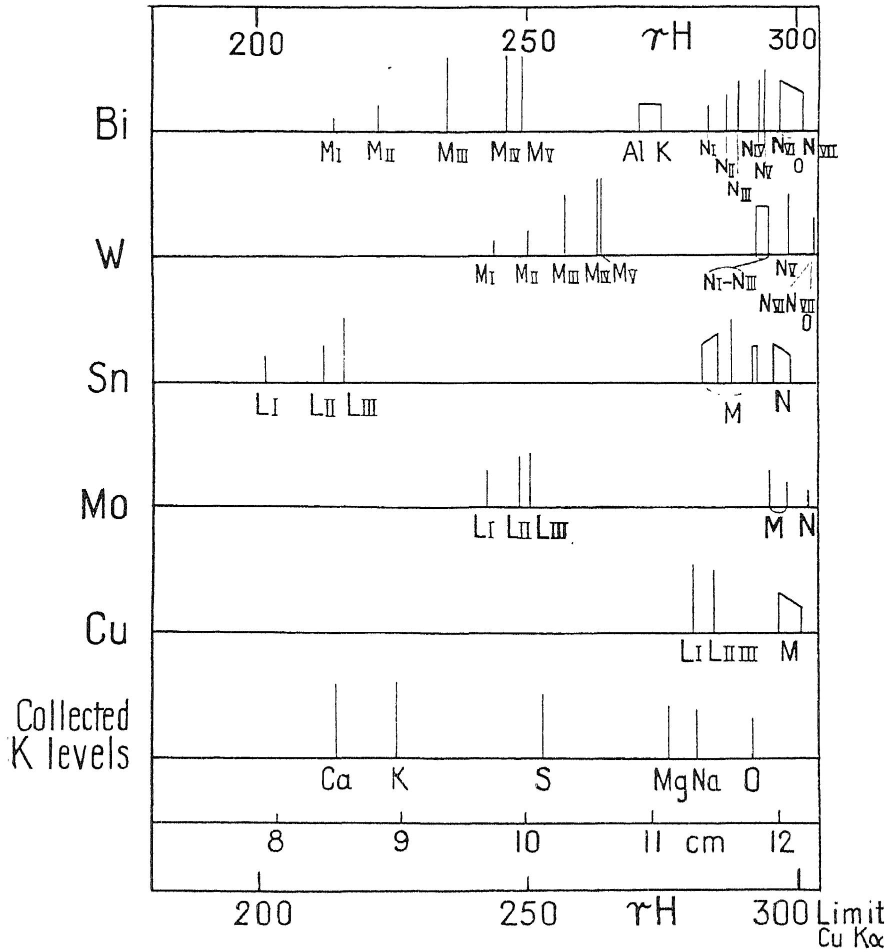


Fig. 4.

In view of what has been said of the method of estimating these intensities, the estimates for individual lines cannot be very accurate, but the general trend of the results is unmistakable. Further, the estimates on lines belonging to the same group, and appearing close together on the plates, cannot be very much in error.

The M and N levels are so numerous and so closely packed on the photographs that it is not possible at present to identify them all with certainty in the lighter atoms, so I shall not discuss their evidence in detail. It is fairly clear, however, that they also show a similar changing over of high intensity from the "softer" to the "harder" sub-groups as we pass down the list.

It is natural to suppose that the conditions approximating most closely to those of the γ ray experiments will be found, in the case of these soft X-rays, in their interaction with the most lightly bound electrons of the target. It has been shown above that it is exactly in this region that an interesting feature of some of Ellis's experiments is reproduced. The present experiments also show the gradual transition from the normal effects in the X-ray regions to the exceptional type found in some of the γ ray regions.

It is impossible to draw any definite conclusion from results obtained with X-rays of a single frequency, but the results are at least suggestive. These experiments provide one of the very few methods of studying the finer details of the interaction between X-rays and different types of bound electrons.

It should also be mentioned in connection with the intensities that in the region investigated the outer electrons contributed quite liberally to the total effect. This was in agreement with a great deal of evidence from the results of ionisation measurements, which cannot, however, be adequately discussed here.

The K Levels of the Light Atoms.

The K levels have been measured for calcium (20), potassium (19), sulphur (16), magnesium (12), sodium (11) and oxygen (8). The corresponding lines are not at all difficult to obtain with the present apparatus, though the falling-off in intensity with the lightest atoms is marked (*cf.* Whiddington, *loc. cit.*). Thus, with a Na_2SO_4 target the intensities of the lines were roughly S : Na : O : : 6 : 5 : 3, though the lighter atoms are present in greater number than the heavier ones.

The numerical values obtained here are of great interest; I have plotted them on a Moseley diagram with Fricke's and other values for comparison (fig. 3). The straight line is drawn through the points taken from X-ray data. It will be seen that my results are consistently high for these elements.

I do not wish to lay too much stress on these measurements, as it is obvious that all the experimental and other errors inherent in the method are enormously magnified in this region. Other data obtained in the same region are, however, in good accord with X-ray data, and I do not think the deviations

can be entirely experimental error. If this is correct, the accepted values of ν/R for the L levels of the light atoms must also be too small.

As exact numerical data for the lower-frequency levels are necessary for the development of the "fine structure" of the Bohr theory* there is obviously need for further experiment. As the present apparatus was not designed for the highest accuracy in this part of the spectrum, any more detailed discussion of the results would be out of place at the present stage.

I have copied a few typical photographs in the diagram (fig. 4); all were taken with the same magnetic field (48 Gauss). The heights of the lines are drawn proportional to the estimated intensities, and the figure gives some idea of the type of variation which has been discussed in the paper.

It is hoped shortly to modify the apparatus and methods, and to extend the measurements into the regions which contain information vital to the development of the quantitative side of the Bohr theory.

In conclusion, I wish to express my thanks to Sir Ernest Rutherford for providing the facilities for this work, and for his continued interest in its progress; and to the Council of the Royal Society for the grant of the Moseley Studentship, which has made it possible for me to resume scientific work. It has been a source of pleasure to me that the work undertaken has been in that branch of physical science which originated in Moseley's classical experiments on the high-frequency spectra of the elements.

* *Cf.* Bohr and Coster, *loc. cit.*

Intensities in the Helium Spectrum.

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(Communicated by Prof. H. A. Wilson, F.R.S.—Received June 5, 1923.)

Merton and Nicholson* made a quantitative study of the distribution of intensities in the spectra of hydrogen and helium under different conditions. Among other things, they studied the distribution of intensities in the helium spectrum as a function of the distance from a flat cathode in a wide vacuum tube. They also investigated the effect of admixture of other gases, and the effect of putting a condenser in parallel with a vacuum tube. The results were extremely interesting; but it seems that, in most cases, the changes were brought about by a simultaneous change in more than one variable, or that they were changes of a kind not capable of simple specification in terms of atomic processes.

Thus when a condenser is put in parallel with a vacuum tube, the energy of impact of the electron on the atom and the density of the current are altered. Moreover, both of these vary rapidly with the time, since the current is necessarily alternating. To account for the observed distribution of intensities under such conditions is a formidable problem when we consider that the quantitative explanation of the intensity of any spectrum line would be a different problem, on any atomic theory, even when the conditions are reduced to the very simplest.

With such considerations in mind, we attempted to study the distribution of intensities as a function of a single fundamental variable. An atom can be put into a radiating state either by the impact of an electron, or by the absorption of radiation. If we confine ourselves to the first mode, the most important variable governing the emission of spectra seems to be the energy of impact of the electron on the atom. Other variables, such as pressure and current density, do have an effect in practice, but these are probably of a secondary character in that they come into play after the atom has been put into a radiating state. The pressure effect may be due to the proximity of atoms modifying the process which has been started in the radiating atom,

* Merton and Nicholson, 'Phil. Trans.,' A, vol. 217, p. 237 (1917); and vol. 220, p. 137 (1919).

while the current-density effect may be due to a modification arising from the electric fields of neighbouring charged atoms and electrons. Under certain conditions of pressure and current density, it may also be possible for electrons to hit ionised or partially ionised atoms* as well as neutral atoms, thus bringing in a second type of radiating system into more or less prominence.

It seems reasonable to imagine a situation in which the pressure is so low and the current density so feeble that further reduction would have no effect on the radiating atoms, and that consequently the surviving, and fundamental, variable would be the energy of impact of the electron on the normal atom. Whether this view as to the part played by pressure and current density be true or not, a study of the changes in the distribution of intensities as a function of energy of electronic impacts on atoms, other variables being held constant, yields interesting results.

An account of a similar research on hydrogen has been published by the authors.† An entirely different apparatus was constructed for the present investigation and the methods improved in a number of ways. The experimental method consists in causing electrons from an incandescent filament to impinge on helium atoms with a definite energy of impact and studying the intensities of the spectrum lines so produced. It will be recognised that the method is almost identical with that used in studying "radiating potentials," in which the interest is confined to the threshold values of the potentials at which the important spectrum lines are excited. This investigation may, therefore, also be regarded as a development of the study of radiating potentials.

Apparatus and Method of Experiment.

The apparatus is shown in fig. 1. It consists of a tube of pyrex glass 45 mm. in diameter. At the end facing the spectrograph, a plane disc of pyrex glass is welded on to the tube. The filament leads, together with the glass rod for keeping the filament taut, are mounted on a glass tube which fits into the main tube by a carefully made ground-glass joint. This is made air-tight by sealing with de Khotinsky cement. As shown in the diagram, the cement between the glass surfaces stops short about 1 cm. from the inside, so that with a continuous flow of gas through the apparatus any contamination from the cement is out of the question. With the exception of this joint, all joints are glass welded to glass or tungsten sealed through glass.

* A partially ionised atom is one in which an outer electron has been displaced from its normal orbit to one of the more remote orbits, which are not occupied when the atom is in its normal state.

† Hughes and Lowe, 'Phys. Rev.,' vol. 21, p. 292 (1923).

Helium from a steel cylinder, in which it was stored under pressure, was passed very slowly through activated coco-nut charcoal in liquid air into a

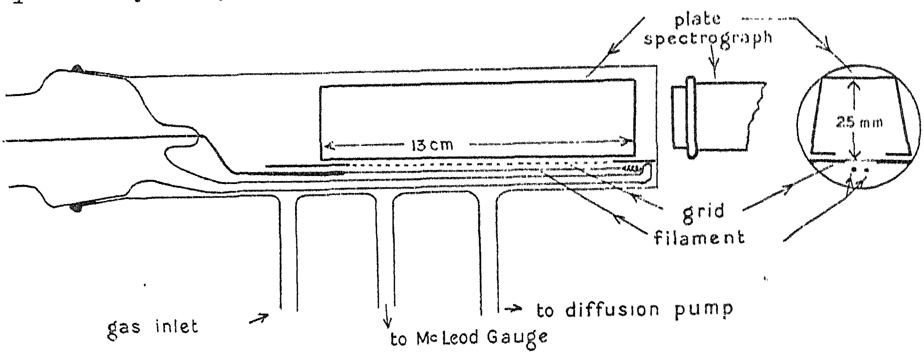

Fig. 1.

100 c.c. reservoir. This purified helium was the stock for several months' work. From here, at atmospheric pressure, it passed through a very fine capillary tube, and (now at low pressure) through a tube of charcoal in liquid air (into the experimental tube) from which it was continuously pumped out by a diffusion pump. The pressure in the experimental tube was exceedingly uniform, no measurable variation being detected in a 24-hour run. U-tubes in liquid air between the apparatus and the diffusion pump, and between the apparatus and the McLeod gauge, kept mercury vapour out of the experimental tube. The helium as it passed through the apparatus was probably extremely pure. No trace of any spectrum line belonging to a possible impurity (mercury, hydrogen, etc.) could be detected on the spectrograms. By the time the final spectrograms were taken, the apparatus had been in continuous use for four months, without once admitting air or any gas other than helium.

Electrons are accelerated from an incandescent filament to a nearby "grid," after which they pass into a field-free space between the "grid" and a "plate." Here they collide with helium atoms, causing them to give out a spectrum. The source of electrons is a 20 cm. length of oxide-coated filament, doubled into an elongated U, with the two limbs parallel and 6 mm. apart. The grid is a set of nickel wires 1 mm. apart, strung across an opening 1 cm. × 10 cm. in a sheet of nickel filling the tube, as shown. The opening is symmetrically above the filament. The "plate" consists of a nickel sheet about 13 cms. long and bent into the shape shown, so that, in cross-section, it is practically a Faraday cylinder. By connecting the plate and grid to the positive end of a battery and the filament to the negative end, electrons from the filament are accelerated up to full speed as they pass through the grid,

beyond which they travel with constant velocity. A microammeter in the plate circuit measures the electron current passing through the grid and caught by the plate. The electron current could be held steady to within 0·3 per cent. by occasionally adjusting the filament heating current. Since no change in the pressure could be noticed, one may conclude that the number of impacts per second between electrons and atoms is constant, and therefore that, as the accelerating potential is altered, any change in the spectrum is due solely to a change in the impact energy.

The potential drop along the filament was about 6 volts, so that a nominal accelerating potential of 34 volts, for example, would mean an accelerating field of 34 volts from one end of the filament and of 28 volts from the other end. This departure from ideal conditions could be avoided by any of the well-known methods used in experiments on radiating and ionising potentials (such as a rotating commutator device, for putting on the accelerating voltage and heating current alternately), but it was not thought necessary at the present stage. It will be advisable in future work, when making a closer examination of the spectrum associated with accelerating voltages lower than 34 volts. With the present arrangement, we could not get enough current through the apparatus below 34 volts.

As has been mentioned before, the ideal way of conducting this investigation would be to work with extremely low pressures and feeble electron currents, so as to approach the limiting case of a spectrum whose character is determined solely by the one variable, the energy of impact. Unfortunately, we are limited by the fact that decrease in the number of impacts per second necessitates greater exposures. Finally, after many preliminary experiments, we decided on using a pressure of 0·0120 mm. and an electron current of 7·20 milliamperes, as being the lowest practicable values to use. An exposure of two hours was made on Wratten panchromatic plates for each accelerating potential. Eight exposures were taken consecutively, so that any one set of spectrograms required nearly 20 hours.

At the pressure of 0·0120 mm., the mean free path of an atom of helium is 1·88 cm., while that of an electron in helium is 10·5 cm. The proportion of electrons passing through the grid and reaching the plate 2·5 cm. beyond without collision is $e^{-\frac{2\cdot5}{10\cdot5}} = 0\cdot788$. The proportion making collisions is therefore 0·212; *i.e.*, only 21 per cent. of the electrons collide between the grid and plate. Of these, it may be shown that approximately 90 per cent. reach the boundary without further collision. The 10 per cent. colliding a second time do so with reduced energy and contribute an intensity distribution

appropriate to a lower accelerating voltage than that actually used. Theoretically, one could lower without limit the proportion of electrons making second collisions, merely by continued reduction of pressure, but in practice a stage is soon reached when the light is too feeble to affect the plates in a reasonable time. Moreover, an appreciable proportion of electrons is reflected, or re-emitted, by the surface. Farnsworth* found that when electrons of 110-volt energy impinge on nickel, roughly 20 per cent. are reflected with energies between 50 and 110 volts. Hence there is no point in reducing the number of electrons making second collisions much below the number reflected from the nickel surface.

Measurement of Intensities.

In some experiments we used a micro-photometer† to measure the density of the lines on the negative. While it does this satisfactorily, it does not give directly the intensity of the spectrum lines themselves. To get the intensity itself, it would be necessary to find the characteristic curve showing the relation between the blackening on the plate and the intensity of the light. It is troublesome business to obtain the characteristic curve under the actual conditions of the experiment. For our final curves we relied on the neutral-wedge method as developed by Merton and Nicholson.‡ (The results with the micro-photometer were in general agreement with those obtained by the wedge method.) A wedge of approximately neutral-grey glass, 7 mm. long (cemented to a clear-glass wedge to avoid deviation), is placed over the slit of a spectrograph. The intensity of the light passing through the slit is decreased by an amount depending on the thickness of the wedge. Since the thickness of the wedge is proportional to the height (h) from the apex, the intensity, I_c of the light passing through may be written as

$$I_c = I_0 \, 10^{ah}$$

where I_0 is the intensity of the light incident on the wedge. Each spectrum line on the photographic plate will therefore fade off in density in accordance with the increasing absorption of light along the wedge. The greater the "height" of the line on the negative, the greater the original intensity. To measure this height accurately, we followed Merton and Nicholson's procedure. Negatives were made on Wratten panchromatic plates. From these, contact

* Farnsworth, 'Phys. Rev.,' vol. 20, p. 358 (1922).

† We have to express our thanks to Dr. P. D. Foote, of the Bureau of Standards, for the design of an improved type of micro-photometer.

‡ Merton and Nicholson, *loc. cit.*

positives were made on Wellington S.C.P. lantern plates. Enlargements were then made on bromide paper through a photo-engraver's ruled Process screen (having one set of rulings instead of the usual two sets at right angles) placed in contact with the paper. The rulings were arranged at right angles to the height of the spectrum lines, so that each line was made up of a series of horizontal streaks 0·01-inch apart. The height of the line was determined by counting to the last visible streak, which could be picked out with considerable certainty, whereas in the absence of the ruled screen it would be difficult to judge exactly where the line faded to nothing. As the enlargements were always made with a constant enlargement ratio, our discussion will be referred to the bromide paper, instead of to the original negative, as in Merton and Nicholson's work.

Let I_c be the critical intensity which is just necessary to make the last visible streak in the spectrum line on the enlargement. For a given spectrum line in any two exposures on the same bromide paper, it may be assumed that the last streak corresponds to the same critical intensity I_c. From a measurement of the heights of any one spectrum line in different exposures, one can compare the intensities of the line under the different conditions of excitation. Let h' and h'' be the heights corresponding to incident intensities I_0' and I_0''. The fundamental formula for the wedge leads to

$$\log_{10} I_0' = \alpha h' + \log_{10} I_c$$
$$\log_{10} I_0'' = \alpha h'' + \log_{10} I_c$$
$$\log_{10} I_0'/I_0'' = \alpha (h' - h'')$$

so that all we need to measure is the difference in the heights of the same line in the different exposures. If the wedge were truly neutral, α would be the same for all wave-lengths. Actually, the density gradient, per mm. of the wedge itself, varied from 0·17 for $\lambda 7065$ to 0·37 for $\lambda 3889$. The calibration was carried out by a method practically identical with that used by Merton and Nicholson.* We cannot compare the actual intensities of two *different* spectrum lines, since the critical intensity I_c which just produces the last visible streak on the bromide paper is determined by the sensitivity of the panchromatic plate for different parts of the spectrum. It would be necessary to determine the sensitivity curve of the plate to get at the actual intensities of the spectrum lines. For our purpose, all we require is the change in intensity in any spectrum line, as the condition of excitation, the energy of impact, is altered.

* Merton and Nicholson, *loc. cit.*

In our actual experiments we used two wedges of different density gradients over different parts of the slit. The lighter wedge took care of all the spectrum lines except λ5016, which was generally so intense that its height on the bromide paper was equal to the height of the wedge image itself. In such cases the photograph through the darker wedge had to be used. The results with the darker wedge could be reduced to those with the lighter wedge by an obvious calibration.

It is a fundamental assumption in the wedge method that the illumination over the slit should be uniform. The length of the slit was parallel to the direction of motion of the electrons. It is clear that as we go away a distance x from the grid, the number of electrons which collide within any small length dx is proportional to $e^{-x/l}\,dx$, where l is the mean free path of the electron. Taking x as 0·7 cm., the length of the wedge, and l the mean free path of the electron at 0·012 mm. as 10·5 cm., $e^{-x/l} = 0 \cdot 93$. This means that we should expect a change of intensity of about 7 per cent. along the length of the wedge. This was checked directly by taking a photograph of the spectrum using the whole length of the slit without any wedges in position. The blackening of several lines on the negative was measured at different distances from one end by the micro-photometer, and the falling-off in density noted.

To get the characteristic curve for a plate, several spectrograms of an ordinary helium tube were taken, the light intensity being cut down in known ratios by Eastman neutral-grey filters. The two plates were developed simultaneously in the same solution. On measuring the blackening by the micro-photometer for the different known intensities, it was possible to conclude that on averaging results from a number of observations, there was a change in intensity of about 9 per cent. along the 7 mm. wedge. This is in satisfactory agreement with the theoretical value. This could have been allowed for, but it was not considered necessary, as in no case did a spectrum line vary under different conditions in height by the full length of the wedge. In most cases, the height of a line (referred to the wedge) would only vary by 2 or 3 mm., so that the correction for lack of uniformity of illumination would be less than 4 per cent. The errors due to non-uniformity of the negatives, the positives and the bromide paper, probably exceed this.

The Results.

Before taking up the experimental results in detail, it is of interest to record that the appearance of the discharge was very different from that of an ordinary helium tube. With accelerating potentials from 230 down to about 45 volts

the discharge was apple green in colour, while from 40 down to 34 volts it was decidedly blue.

The wedges were so fixed over the slit that about 0·5 mm. of the slit was not covered by either wedge, permitting us to get a more intense spectrum than could be got through the wedges. The following known arc lines of helium were identified (Fowler's notation) :—

Singlet System.

Principal (1S—mP).		*Diffuse* (1P—mD).		*Sharp* (1P—mS).	
m	λ	m	λ	m	λ
2	5016	2	6678	3	5048
3	3965	3	4922	4	4438
		4	4388	5	4169
		5	4144	6	4024 (?)
		6	4009§		

Doublet System.

Principal ($1\sigma-m\pi$).		*Diffuse* ($1\pi-m\delta$).		*Sharp* ($1\pi-m\sigma$).	
m	λ	m	λ	m	λ
2	3889	2	5876	2	7065§
		3	4471	3	4713
		4	4026	4	4121

The lines marked § were too weak to show through any part of the lighter wedge. The line $\lambda 4024$ of the Singlet-Sharp Series was probably merged with $\lambda 4026$ of the Doublet-Diffuse Series, but it is extremely likely from the way in which the intensity falls off in the two series that $\lambda 4026$ accounts for most of the intensity.

According to Bohr's theory of the helium atom, and to Compton, Lilly and Olmstead's experiments,* the enhanced spectrum of helium should appear even in moderate discharges, whenever the energy of impact of the electron on the atom exceeds about 80 volts. In agreement with this, we found that the enhanced line $\lambda 4686$ [4N $(1/3^2-1/4^2)$] appeared very faintly with electron

* Compton, Lilly and Olmstead, 'Phys. Rev.,' vol. 16, p. 289 (1920).

energies of 85 volts, noticeably with 110 volts, and that it was relatively quite strong at 210 volts. We also found some very faint lines at 210 volts, which corresponded in position with the lines λ5412, λ4859, and λ4542 of the Pickering series [$4N\ (1/4^2 - 1/m^2)$]. Three other extremely faint lines appeared only at 210 volts, viz., λ4275, λ4260, and λ4575. (These are possibly open to an error of ± 5 units, as we used a wide slit for our intensity measurements.) They do not appear to belong to any probable impurities. Thus, not the slightest trace of Hα or Hγ could be found. (Hβ would almost coincide with the faint line λ4859, which we are inclined, however, to regard as a helium line.) No trace of any of the strong lines of mercury could be detected. The unknown lines referred to appeared every time with 210 volts. In some cases, the 210 volt exposure came at the end of a 20-hour series of exposures, during which the pumps and liquid air had been in action continuously and during which the filament had been maintained steadily at a dull-red heat. It seems hardly likely that the lines could be attributed to impurities.

The curves showing the final results are obtained from two negatives, on each of which were four exposures. These were obtained with accelerating potentials of 110, 34, 40 and 65 volts, and with 110, 85, 50 and 210 volts, in the order named. A consideration of the method of measuring the photographic intensities shows that it is necessary to have one voltage in common for both plates, so as to link up the data of the two plates. A peculiarity of the second plate was that the 85 volt exposure gave points on the curves which were all lower by approximately 0·06 (the unit is the logarithm of the photographic intensity) than the smooth curve through the rest of the points. This may have been due to an error in timing this particular exposure. Hence for plotting the curves, we have added 0·06 to every 85-volt result, but for purposes of record, we have indicated on every curve the actual unaltered value of the ordinate at this voltage.

Owing to the great changes in the intensities of some lines, it is more convenient to plot the logarithm of the photographic intensity than the photographic intensity itself. In plotting the logarithm against the voltage, $\log I_c$ in equation (1) is arbitrarily put equal to zero. This is justified as the ultimate purpose of the curves is to give the *ratio* of the intensities of a spectrum line when excited under different conditions, and this follows directly from the *difference* in the heights of the same line in successive exposures from the equation

$$\log I_0''/I_0' = \alpha\,(h''-h')$$

in which I_c does not appear.

The most important result of this investigation is that the shape of the curve for any spectrum line is characteristic of the series to which it belongs. Indeed, it is possible that we could apply the method to suggest a classification into series, in the case of a gas whose spectrum has not yet been resolved into series.

Fig. 2 gives curves for two lines of the Principal Series of the Singlet System. Both lines are characterised by a great increase in intensity as the accelerating

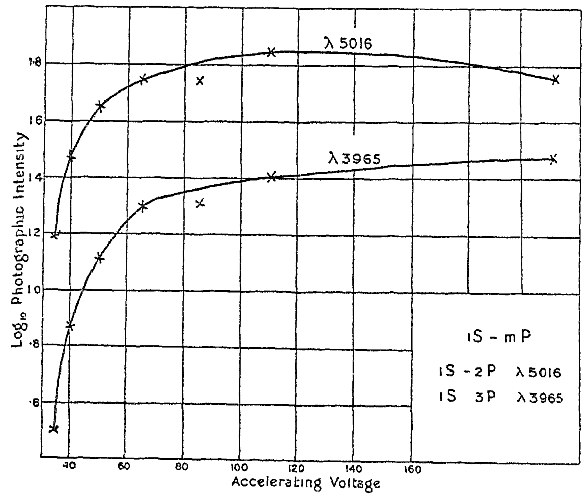

FIG. 2.

potential is increased from 34 to about 80 volts. (The ordinates of $\lambda 3965$, for example, indicate a change in intensity of almost tenfold.) It will be observed that the increase in the shorter line $\lambda 3965$ is relatively greater than in $\lambda 5016$ at the higher voltages. Fig. 3 shows the curves for the Diffuse Series of the

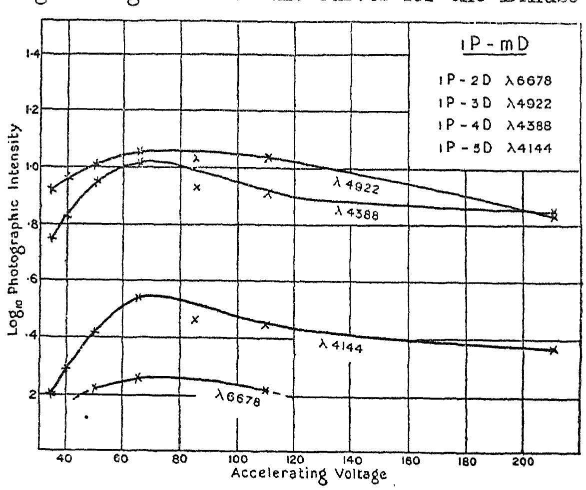

FIG. 3.

Singlet System. As in the Principal Series we find an increase (though considerably smaller) as we go from 34 volts up. This series, however, has a maximum at about 75 volts. The rise from 34 volts, it will be noticed, gets progressively steeper as we pass from λ6678 to the higher members in the series. Fig. 4 gives the curves for the Sharp Series of the Singlet System. After a small initial rise, there is a gradual fall with increasing voltage.

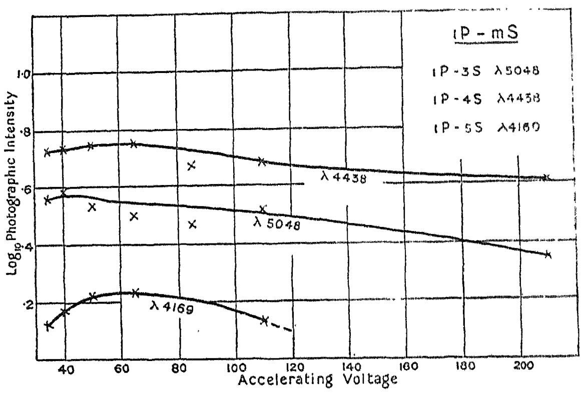

Fig. 4.

The lines in the Doublet System are sharply distinguished from those in the Singlet System by a rapid fall in intensity with increasing energy of impact. Since we have only one line in the Principal Series, we have plotted its curve on the same diagram (fig. 5) as the curves for the Sharp Series. Both series show a rapid fall, which is more marked for the Sharp Series than for the

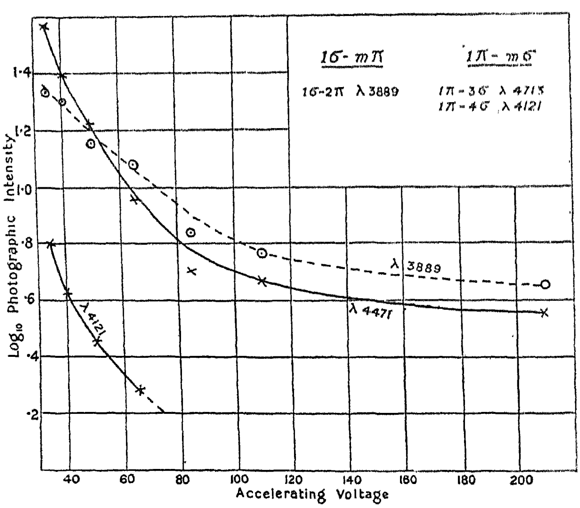

Fig. 5.

Principal Series. In fig. 6 we have the curves for the Diffuse Series of the Doublet System, in which the fall of intensity is considerable, though less than

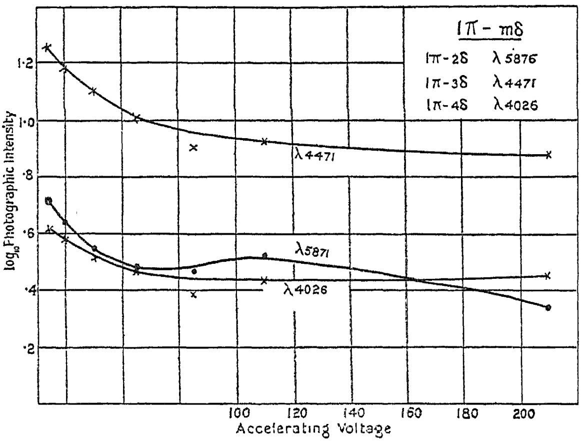

Fig. 6.

for the other two series. (We are inclined to believe that the irregularities in $\lambda 5048$ and $\lambda 5876$ are accidental rather than real.)

It may not be superfluous to emphasise here that these curves are of no use for comparing the intensity of one spectrum line with another, since we have not allowed for the sensitivity of the plates at different parts of the spectrum. What the curves do give is a comparison between the variations in one spectrum line with the variations in another spectrum line.

Discussion.

This research was planned with the intention of investigating, as closely as conditions would allow, the effect of varying the energy of impact between electrons and normal atoms. It is, therefore, desirable to estimate how closely this ideal is realised, that is, to estimate whether collisions between electrons and ionised, or partially ionised, atoms form an appreciable fraction of the total number of collisions. Effects arising from impact of electrons on atoms while still ionised or partially ionised from some previous encounter or absorption of radiant energy have been termed "cumulative" effects, to distinguish them from the ordinary effects arising from collisions with normal atoms. Our knowledge of cumulative effects is due largely to Prof. K. T. Compton* who has developed methods for quantitative computation. When an electron

* K. T. Compton, 'Phys. Rev.,' vol. 20, p. 283 (1922); 'Phil, Mag.,' vol. 45, p. 750 (1923).

hits an atom already ionised or partially ionised by a previous impact, the cumulative effect is referred to as a *Successive Impact* effect, while it is called a *Photo Impact* effect when the electron hits an atom ionised or partially ionised by the absorption of radiation.

Successive Impact.—For simplicity we can assume that the electron stream passing through the grid is uniformly distributed over the area of the opening, viz., 1 cm. $\times$ 10 cm. = 10 sq. cm. Let

i = current passing through grid per unit area ($0{\cdot}72 \times 10^{-3}$ amp.).

n_0 = number of electrons passing through grid per unit area per second.
$= i \div$ electronic charge (in coulombs).
$= (6{\cdot}29 \times 10^{18}) \times i$.

n = number of electrons colliding with atoms per cm. of path per second.

l = mean free path (cm.) of an electron in helium at press. p (mm.).
$= 0{\cdot}126/p$.

$n = n_0(1-e^{-1/l})$.
$= n_0 1/l$ approximate, since l at the pressure ($0{\cdot}012$ mm.) is $10{\cdot}5$ cm.

$$= n_0 \frac{p}{0{\cdot}126} = \frac{6{\cdot}29 \times 10^{18}}{0{\cdot}126} \times ip = 5{\cdot}0 \times 10^{19}\, ip.$$

This will measure the number of collisions per c.c., since n_0 refers to the number passing through unit area. Now the number of atoms per c.c. at the pressure p (mm.) is

$$N_0 = (3{\cdot}55 \times 10^{16}) \times p.$$

The ratio Q of the number of atoms struck by electrons per c.c. per second to the total number of atoms per c.c. is n/N_0.

$$= \frac{(6{\cdot}29 \times 10^{18})}{0{\cdot}126}\, i.p. \div (3{\cdot}35 \times 10^{16}) \times p$$

$$= (1{\cdot}40 \times 10^{3}) \times i$$

In our experiment $i = 0{\cdot}72 \times 10^{-3}$; therefore

$$Q = 1{\cdot}01.$$

Since the mean free path of an atom at this pressure is $1{\cdot}88$ cm., which is of the order of the distance across the apparatus, we may assume as a first approximation that an atom struck by an electron will often reach the walls without collision, or certainly will do so without more than one or two collisions. The time taken therefore will be of the order of the diameter of the apparatus, $2{\cdot}5$ cms., divided by the molecular velocity $1{\cdot}25 \times 10^{5}$ cm./sec., or $2{\cdot}0 \times 10^{-5}$ second. As we have seen above, since any individual atom receives an impact

about once per second, the chance of it being struck a second time before it reaches the walls is as $2 \cdot 0 \times 10^{-5}$ to 1, or 1 in 50,000. It seems natural to assume that whenever an ionised atom reaches the metal boundary it will be neutralised and become a normal atom, and hence that the chances of an electron hitting an atom while ionised is negligibly small. Now, as mentioned in the next paragraph, the "life" of a partially ionised atom (*i.e.*, the time interval between excitation and return to normal) is of the order of 10^{-5} second, so that the chance of a second impact on a partially ionised atom is much smaller even than that of an impact on an ionised atom.

Photo Impact.—There is now satisfactory evidence to show that resonance radiation produced in a gas, especially when the pressure is appreciable, does not immediately pass out of the gas, but escapes by a process of absorption and re-emission by successive atoms.* It is easily realised therefore that the rate of escape of radiation depends really on the "life" of a partially ionised atom, *i.e.*, on the time the quantum of radiation is held in the atom between its absorption and re-emission. If atoms are struck by electrons while partially ionised they will give out a spectrum with a different distribution of intensity from that given out by an impact on a normal atom. It is, therefore, necessary to calculate the chance of an atom being struck while partially ionised by the absorption of radiation. We shall follow Prof. Compton's method of computation closely. It is assumed that the radiation may be treated as though it were in quanta which diffuse out of the gas precisely as material particles would. This, as Compton points out, may be regarded merely as a formal method for computation, it does not necessarily bind one to a quantum theory of transmission.

The intensity of a beam of light is reduced by absorption according to the equation $\mathrm{I} = \mathrm{I}_0 e^{-\alpha x}$ while the number of particles passing through a gas in a parallel beam falls off according to the law $\mathrm{N} = \mathrm{N}_0 e^{-x/\lambda}$ where λ is a mean free path. A comparison of the two equations suggests that $1/\alpha$ may be regarded as equivalent to a mean free path. If τ be the time during which a quantum is held in an atom (*i.e.*, the "life" of a partially ionised atom) then the average speed with which the quantum travels is $\bar{c} = \lambda/\tau = 1/\alpha\tau$. The escape of quanta from a gas may be calculated from the diffusion equation of the Kinetic Theory of Gases, viz.,

$$\iint \mathrm{D} \frac{d\mathrm{N}'}{dn} d\mathrm{S} + \iiint \mathrm{R}\, dxdydz = 0,$$

* Horton and Miss Davies, 'Phil. Mag.,' vol. 44, p. 1140 (1922); Compton, 'Phys. Rev.,' vol. 20, p. 283 (1922).

where N' = No. of quanta (= no. of partially ionised atom) per c.c. at any place.

n = outward normal to element of area dS.

R = rate of production of quanta per unit volume.

$D = 1/3\ \lambda\bar{c} = 1/3\ 1/\alpha\ 1/\alpha T$.

To apply to our case, let us consider a sphere of radius a within which quanta are being produced uniformly at a rate which cannot exceed the number of collisions between electrons and atoms. If we take the sphere so that its radius is as big as the largest dimension of the region ($10 \times 1 \times 2\cdot 5$ cm.) in which our atoms are being struck by electrons, we shall over-estimate the number of quanta produced per c.c. The metal walls may be assumed to have a negligible reflection coefficient for the radiation capable of partially ionising helium. Since our assumption is one of spherical symmetry, for any sphere of radius r within the sphere of radius a, the general equation reduces to

$$D\, dN'/dr 4\pi r^2 + R4/3\pi r^3 = 0$$

$$D\cdot N' + R/6 r^2 = K \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

For any sphere outside the sphere of radius a, we have

$$D\, dN'/dr\ 4\pi r^2 + R4/3\ \pi a^3 = 0$$

$$D\cdot N' + R/3\,(a/r)^3 = K' \quad \ldots\ldots\ldots\ldots\ldots (2)$$

At ∞, $N' = 0$, $1/r = 0$, therefore $K' = 0$.

Over the boundary a, (1) and (2) must agree; hence

$$D\cdot N' = R/6\,(3a^2 - r^2).$$

Now the maximum value of N' occurs at the centre

$$N'_{\text{max.}} = Ra^2/2D = 3/2\ Ra^2\alpha^2\tau.$$

The number of quanta produced per second cannot exceed the number of impacts between electrons and atoms. Hence $R \not> (5 \times 10^{19}) \times ip$ (numerical value from previous paragraph on *Successive Impacts*). There is much uncertainty as to what values of α and τ to take. No experiments have ever been made to determine α for any resonance line except for $\lambda 2536$ for mercury. R. W. Wood's experiments on $\lambda 2536$ indicate that $\alpha = (1\cdot 48 \times 10^3) \times p$ where p is the pressure in mm. Wien found τ to be of the order of 10^{-8} second for the visible lines in the hydrogen and oxgyen spectra. As there is no information available as to the value of these constants for the resonance radiation of helium, we shall use these numerical values (as Compton has done) merely to get the roughest idea of the order of N'.

$R \not> 5 \times 10^{19}\, ip$, $a = 5$ cm., $\alpha = 1\cdot 48 \times 10^3\, p$, $\tau = 10^{-8}$; sec.

Therefore $N' \not> 4 \times 10^{19}\, ip^3$.

The number of atoms per c.c. is $N_0 = (3 \cdot 55 \times 10^{16}) p$. Hence the ratio of partially ionised atoms to normal atoms is

$$\frac{N'}{N_0} \not> \frac{4 \times 10^{19} ip^3}{3 \cdot 55 \times 10^{16} p} = 1 \cdot 1 \times 10^3 ip^2.$$

In our experiments, $i = 0 \cdot 7 \times 10^{-3}$ amp., $p = 0 \cdot 012$ mm. Hence

$$N'/N_0 \not> 1 \cdot 2 \times 10^{-4}.$$

In view of the fact that wherever we have introduced simplifications we have liberally overestimated N′, it may be concluded that, with the assumed values of α and τ, the number of partially ionised atoms is negligible compared with the number of normal atoms.

Hence the distribution of intensity in the spectrum may be considered as resulting from the impact of electrons on normal atoms. Moreover, we can attribute the luminosity to partially ionised atoms and not to any extent to re-combination between electrons and ionised atoms. It was shown in the paragraph on *Successive Impacts* that the chances of a collision between a primary electron and an ionised atom, while the atom is travelling to the metal boundary, are negligibly small. The electrons released per second from atoms in the process of ionisation cannot exceed numerically the number of primary electrons shot into the gas, and as the mean free path of the electron is much larger than the diameter of the apparatus, the chances of re-combination between such secondary electrons and positive ions will not be appreciably bigger than the chances of collisions between primary electrons and ions. These considerations, therefore, point strongly to the conclusion that, under our experimental conditions, we are studying the distribution of intensities under comparatively simple conditions of excitation, viz., that the light is due only to partial ionisation resulting from the impact of electrons on normal atoms.

This suggests the clearly defined theoretical problem of calculating the statistical distribution of displacements of the electrons to the various energy levels in the helium atom, as a function of the energy of impact of the electron on the atom.

Recent views of the helium atom attribute the Doublet System (the ortho-helium spectrum) to transitions between different energy levels when the two electrons of the atom lie in coplanar orbits, while the Singlet System (the parhelium spectrum) is due to transitions between crossed orbits.* The

* Lande, 'Phys. Zeits.,' vol. 20, p. 228 (1919); vol. 21, p. 114 (1920); Franck and Reiche, 'Zeits. f. Phys.,' vol. 1, p. 154, 1920; Foote and Mohler, 'The Origin of Spectra,' p. 71.

absence of any combination lines between the two systems implies that transitions cannot take place from a crossed-orbit arrangement to a coplanar-orbit arrangement, nor *vice versa.* The energy levels corresponding to the two systems, so far as the spectrum lines studied here are concerned, seem to interlace each other at random. It is evident that the higher impact energies do not mean an indiscriminate filling-up of the higher energy levels. The higher impact energies lead, in most cases, to displacements to the more remote orbits in the crossed-orbit atom, but in the coplanar-orbit atom the displacements to the outer orbits become *less* plentiful as the impact energy is increased.

It should be mentioned that the impact energy, even with our lowest accelerating potential (34 volts), is considerably more than the minimum energy required to ionise a helium atom (25 volts). It does not, of course, follow that all impact energies above 25 volts ionise the atom; the nature of the impact may determine whether complete or partial ionisation takes place.

Effects of Change of Pressure and Change of Current.

According to the foregoing discussion, the luminosity should be attributed to collisions between electrons and normal atoms, and not to any measurable extent to cumulative effects. It is to be expected, therefore, that the intensity of the radiation should be proportional to the number of impacts between electrons and atoms, provided that each impact could be regarded as an independent event. In the experiments recorded, we worked with as low a pressure and as feeble a current as would enable us to measure the intensity of a sufficient number of lines in eight consecutive exposures of two hours each. There was not much room for a further reduction in luminosity, either by decreasing the electron current or by decreasing the pressure. However, we made some rough preliminary measurements on the effect (1) of reducing the pressure from 0·0120 to 0·00437 mm., the current remaining constant, and (2) of reducing the current from 7·2 milliamperes to 0·25 milliamperes, with the pressure constant. The number of collisions is reduced by the pressure change from 1 to 1/2·75, while the current change reduces it from 1 to 1/2·90, giving approximately the same reduction. The accelerating potential was 40 volts in each case. The reduction in intensities of such lines as could be measured is given in the following table—

Change in Number of Collisions.		*Pressure Change* = 2·75.	*Current Change* = 2·90.
1S—2P	λ5016	6·0	2·4
1S—3P	λ3965	> 8·9	2·3
1P—3D	λ4922	4·6	4·1
1P—4D	λ4388	3·8	4·2
1P—4S	λ4438	4·0	4·2
1σ—2π	λ3889	3·2	3·2
1π—3δ	λ4471	4·9	3·9
1π—3σ	λ4713	5·1	5·1
1π—4σ	λ4121	3·6	3·8

Although the accuracy of these results is not as high as in the experiments previously described, it is very evident that in the case of most of the lines the intensity is far from being proportional to the number of collisions. Thus, the intensity of λ5016 decreases sixfold, when a change in *pressure* decreases the number of collisions 2·75 times ; while its intensity decreases only 2·4-fold when a change in the *electron current* decreases the number of collisions 2·9 times. The table suggests the following inferences :—For infinitely small currents, the Principal Series of both Systems (1S—mP and 1σ—$m\pi$) would stand out relatively stronger than the other two series. For infinitely low pressures 1σ — 2π would stand out relatively strongest, while 1S — mP would disappear first. (Results having the same tendency were obtained when we carried out the pressure change and the current change with accelerating potentials of 110 volts, the lines available, however, being fewer.)

It must be emphasised that these are only rough preliminary results. Our experience shows that it is not possible to make rapid progress in this direction with our present equipment. It will be necessary to use a spectrograph of larger light-gathering power, faster plates, etc., to compensate for the loss in luminosity as the pressure is decreased.

It is difficult to account for the unexpected changes in the intensities of the lines as the number of collisions is reduced. The discussion of cumulative effects seems to rule out the possibility of any appreciable amount of luminosity arising from impacts between electrons and ionised or partially ionised atoms at the pressure and current used. (As Compton points out, however, the values of the important constants in his theory of photo-impact ionisation unfortunately are only the roughest approximations.) These calculations led us to expect that our conditions were sufficiently simplified to yield a

proportionality between the intensity of a line and the number of impacts. This, however, is not the case experimentally. It would seem, therefore, necessary to conclude that the transitions from one energy level to another within the atom after having been struck by an electron are, to some extent, affected by the proximity of other atoms (the pressure effect) and by the proximity of ions or electrons (the current effect). In the latter case the electric field from an electron or an ion might well exercise some effect on the transitions taking place in a neighbouring partially ionised atom. These preliminary results on the effect of reducing the number of collisions do not affect the results of changing the energy of impact, keeping all other variables constant, beyond indicating that the conditions of excitation are still not ideally simple.

Summary.

The distribution in intensities in the helium spectrum, when excited by impacts between electrons and atoms, has been studied as a function of the energy of impact of the electrons, all other variables being held constant. The energy of impact varied from 34 volts to 210 volts.

The outstanding result of the work is that the curve showing the intensity of any spectrum line as a function of the energy of impact is characteristic of the series to which it belongs. The intensities in the Doublet System all decrease rapidly as the energy of impact is increased from 34 volts. The rate of decrease is greatest for $1\pi—m\sigma$ and least for $1\pi—m\delta$. The Principal Series, 1S—mP, of the Singlet System is characterised by a very great increase in intensity as the energy of impact is increased from 34 volts up to about 80 volts, beyond which there is little change. The lines of the Diffuse Series, 1P—mD, all show a maximum at about 75 volts, the rise to maximum being progressively greater the higher the term number of the line. The lines of the Sharp Series, 1P—mS, after a small initial rise to 60 volts, decrease slightly.

Part of the equipment for this research was purchased by means of a grant from the Honorary Advisory Council for Scientific and Industrial Research of Canada.

On a Null Method of Measuring the Gyro-Magnetic Ratio.

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(Communicated by Prof. A. P. Chattock, F.R.S. Received July 24, 1923.)

It was first shown by O. W. Richardson† that if the magnetic properties of ferro-magnetic substances are due to the rotation of the electron orbits of the atom, then a change M in the magnetic moment of a specimen of such material should be accompanied by a change in the angular momentum U given by

$$\frac{\mathrm{U}}{\mathrm{M}} = \frac{2m}{e},$$

where m and e are the mass and charge of an electron respectively.

Several experimenters have shown that the value of the ratio is approximately one-half that expected on the above theoretical grounds. Recently work in this University‡ has indicated that within the limits of experimental error the value of the ratio is exactly one-half for iron and nickel. The present work was undertaken with the object of checking these results, and further, of determining the ratio for the Heusler alloys. Owing to the time lag which accompanies the magnetisation of these alloys, the only method which has so far proved suitable is that of Barnett, in which the change of magnetic moment is produced by rotation. In an advance note§ it is stated that for certain ferro-magnetic substances, including Heusler alloys, the ratio is one-half, but the results are "within 10 per cent. or less."

In the present method a thin iron rod L is suspended by means of a German-silver wire G from the torsion head T (*see* figure), so that the rod lies symmetrically along the axis of the vertical magnetising helix H, which can be supplied with current from an A.C. generator. To the lower end of the rod is attached an aluminium wire D of about 1 mm. diameter, which carries the small mirrors M and a number of short magnetised needles N. These needles are adjusted to be midway between a pair of small Helmholtz coils B B. A helix J coaxial with the specimen L is fixed inside the magnetising helix H.

* The work described in the present paper was to have been a joint research, but owing to unforeseen circumstances the bulk of it was carried out by one of us.—W.S.

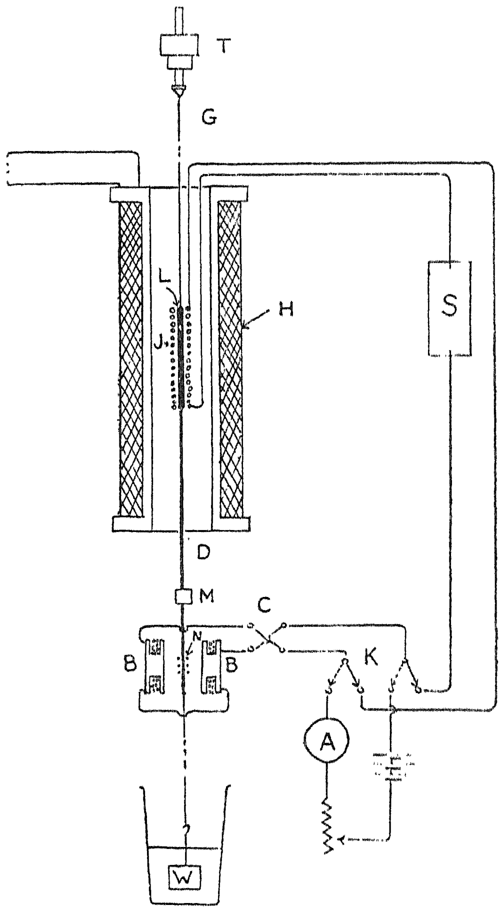
† O. W. Richardson, 'Phys. Rev.,' vol. 26, p. 248 (1908).

‡ Chattock and Bates, 'Phil. Trans.,' A, vol. 223, p. 257.

§ S. J. Barnett and L. H. J. Barnett, 'Phys. Rev.,' vol. 20, p. 90 (1922).

The coils B B can be placed in series with a resistance box S and the induction helix J, a commutator C being included to reverse the current when necessary. The switch K allows a known current to be passed through B B. A fine silk thread carrying a 200 grm. weight W immersed in oil is attached to the lower end of the aluminium wire.

When an alternating current flows in H, the magnetism of the specimen



is periodically reversed, and the gyro-magnetic effect (hereafter called the R effect), together with a number of disturbing couples, tends to make the system oscillate about its vertical axis. It is shown below that the effects of these disturbing couples may be eliminated. Assuming for the moment that they are negligible, then the amplitude is wholly due to the R effect, and will be a maximum when the frequency of the impressed A.C. is equal to the natural frequency of oscillation of the system. Both the R effect and the current

induced in J depend upon the rate of change of magnetism, and are consequently in the same phase, providing the inductive lag in the current can be made negligible. The induced current in J flows through the coils B B and the resistance S. The latter is adjusted so that the momentum delivered to the system by the action of the current in the coils B B on the magnets N is equal and opposite to that due to the R effect; in other words, the oscillations are reduced to zero.

Let I be the number of lines of force which cut the induction helix J when the moment of the specimen changes by M, then

$$\mathrm{I} = 4\,\pi\,\frac{\mathrm{M}}{l} \times (\text{number of turns on J}).$$

If n is the number of turns per cm. on the helix J, which is the same length l as the specimen, then

$$\mathrm{I} = 4\,\pi\,\mathrm{M}n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Let Γ be the couple acting on the magnets N due to unit current in the coils B B. When the R effect is completely neutralised, then the angular momentum delivered to the magnets N, due to a change M in the magnetic moment of the specimen, is equal to

$$\mathrm{U} = \Gamma\,\frac{\mathrm{I}}{\mathrm{S}_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where S_0 is the total resistance in the induction helix circuit.

If a steady deflection ϕ is produced when a known direct current i flows through B B, then

$$\Gamma i = c\phi \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where c is the torsion constant of the suspension.

Eliminating Γ and I from equations (1), (2) and (3), we get

$$\frac{\mathrm{U}}{\mathrm{M}} = \frac{4\pi n c\,\phi}{\mathrm{S}_0 i}.$$

It will be seen that all the quantities involved in the above expression for the ratio U/M are capable of accurate measurement. Experimenters who previously used resonance methods were confronted with the difficulty of the accurate determination of the frequency of oscillation and its maintenance during the measurement of the maximum amplitude of vibration. But it will be seen that the above expression contains no term involving the frequency of oscillation. Moreover, we do not need to measure the maximum amplitude of vibration, as our method is merely concerned with its reduction to zero, and any lack of complete resonance will result only in a decrease of sensitiveness

and will not cause an actual error in the determination of the ratio; it is sufficient to keep the frequency of oscillation constant and approximately equal to the natural frequency of the system. Further, we have not to measure directly the magnetic moment of the specimen or the small moment of inertia of the system, and the damping factor only affects the method in so far that it limits the amplitude of vibration and therefore the sensitiveness of the method. Lastly, the necessity of having to assume that the A.C. produces magnetic saturation equal to that obtained by steady current methods is obviated, thus admitting of application to the Heusler alloys.

Description of Apparatus.

The magnetising helix was wound on an ebonite tube, 44·3 cm. long and 6·3 cm. external diameter, provided with stout flanges 10·5 cm. in diameter. It comprised 1880 turns of No. 22-gauge double cotton-covered copper wire in six layers, each layer being carefully insulated from the next. The helix was set up vertically, and each end was adjustable laterally by four horizontal brass screws (not shown in figure) mounted on horizontal platforms and bearing against the ebonite flanges.

The induction helix J consisted of a single layer of 460 turns of No. 34-gauge double silk-covered copper wire wound on a uniform glass tube of external diameter of 1 cm. Two circular ebonite flanges (sliding easily inside H) were cemented to the tube at the ends of the induction helix, and two screws and a spring projecting from the sides of each flange served to keep the latter in position inside the magnetising helix. The upper end of the glass tube projected above the top of the latter helix and served to indicate the position of J.

Each Helmholtz coil B consisted of about 1,200 turns No. 34-gauge double silk-covered copper wire, wound on an ebonite spool 2·5 cm. in external diameter and 2 cm. in length. These were rigidly connected together with ebonite supports. Two horizontal glass rods passing through holes bored in the spools served to carry the coils and to maintain their planes vertical. Lateral and vertical adjustments could be made by sliding the spools along the rods and by altering the position of the clamps which held the rods.

The torsion head consisted of a flanged brass cylinder which turned in a well-fitting brass collar mounted on a horizontal platform. Adjustments could be made in a horizontal plane, so that the axis of rotation of the torsion head could be made coincident with that of H.

The source of alternating current was a four-pole shunt-wound generator,

directly coupled to a direct current motor driven by storage batteries. The frequency was variable between 24 and 80 cycles per second. A Crompton-Robertson vibrator, used in conjunction with a stroboscopic disc fixed to the end of the generator shaft, served to indicate the frequency of rotation. By the use of movable loads on the vibrator bars, stationary patterns could be obtained for any frequency over the experimental range.

The plane mirrors M were 3×4 mm. and were placed back to back on opposite sides of the aluminium wire with their planes approximately parallel. The motion of the system was observed by a lamp and scale, the latter usually being about 65 cm. from the mirrors. An ordinary metal-filament lamp was used as source and gave an image not more than $0 \cdot 2$ mm. broad.

The magnet system N consisted of two sets of fifteen steel needles, each about 3 mm. long, rigidly cemented to pieces of mica, which in turn were fixed to opposite sides of the aluminium wire. The dimensions of the latter were so chosen that its torsion constant was very great compared with that of the suspension.

Elimination of Errors.

When an alternating current is passed through the magnetising helix, the phase of the magnetism induced in the specimen will always lag a little behind the current. The R effect produced will be 90 degrees out of phase with the alternating magnetism. The neutralising current depends on the rate of the change of magnetism, and is therefore in phase with the R effect, unless the self-induction in the induction helix circuit is sufficient to cause an appreciable lag. The reactance of the helix J and coils B B was small compared with the large non-inductive resistance S in circuit (usually of the order 3,000 ohms), so that this lag must have been negligible in our experiments.

We have now to consider the various errors and the methods of elimination.

§1. In the first place, the horizontal component of the earth's magnetic field acts upon the changing horizontal component of the specimen's magnetism and gives rise to a couple in quadrature with the R effect. This can only produce an apparent increase in the magnitude of the latter, so that by neutralising the earth's horizontal field until the resonance amplitude is a minimum this error may be eliminated. For this purpose two vertical rectangular coils, each of 250 turns and 3×4 feet, were set up with their planes parallel and about 10 inches apart, placed approximately at right angles to the magnetic meridian. Any residual east-west component of the earth's

field was at first neutralised by rotating these coils, but it was later found more convenient to use a small current flowing in two similar coils of 25 turns each with their planes parallel to the magnetic meridian.

§2. The horizontal component of the changing current in the magnetising helix will act upon any permanent magnetism of the specimen, and its effect will be in phase with the changing current, *i.e.*, nearly in quadrature with the R effect. It can be resolved into two components, one in phase and the other in quadrature with the R effect. The second component can only cause an increase of the amplitude, and this will be destroyed along with the adjustments described in § 1. The first component may effect an increase or decrease of the resonance amplitude, such that if in one position the amplitude is increased, it will be decreased by a corresponding amount when the specimen is rotated through 180 degrees. In any case it may be made extremely small by proper adjustment of the helix to the vertical, and by careful centering of the specimen.

The magnet needles N will be acted upon by any stray horizontal field from the helix H. This effect can obviously be minimised by placing the needles a great distance from the magnetising helix, but this is not practicable, and we therefore placed a coil of large area in series with H and below it in such a manner that the field of the coil opposed that of H in the intervening space. By means of a small magnetometer needle hung on a fibre coaxial with H, the region of zero horizontal field was found, and the needles N were mounted on the aluminium wire in this region.

The Helmholtz coils must be so situated that no disturbing currents are induced in them by the field of the helix ; this was arranged by connecting the coils directly to a ballistic galvanometer and adjusting their position until no deflection was observed when a heavy current was suddenly reversed in the helix H.

§3. The alternating horizontal component of the helix may also cause an effect by its action upon the alternating component of the specimen's magnetism. This effect may be resolved into two components, one of which will always result in a steady displacement of the zero of the specimen, but this was never observed. The other component may be sufficiently powerful to produce forced oscillations of double the frequency of the R effect, in which case it will be impossible to bring the system to rest. This was very occasionally observed and was eliminated by re-centering the specimen.

No disturbing effect of the fundamental frequency could arise due to the asymmetry of the current from the generator, as any asymmetry in the

changing magnetism of the specimen is impressed upon the current in the coils B B.

§4. It remains to consider the errors peculiar to the use of the induction helix J. In the first place, we only wish to utilise the E.M.F. due to the changing magnetism and not to the changing current. Hence to cut the least number of lines due to the changing current, the helix J should be made as narrow as possible, the minimum internal diameter of the glass tube being limited by the fact that the magnets and mirrors must pass through without danger of touching the sides. In addition, we introduced a compensating coil F (not shown), in series with the coils J and B B, the coil F being coupled to a coil D inserted in the main magnetising circuit. With the help of a ballistic galvanometer temporarily introduced into its circuit, the position of F was adjusted until the reversal of a heavy direct current in D and H produced no deflection of the galvanometer when the specimen was absent. The two coils F and D then remained in position throughout each experiment.

In the second place, the helix J will not cut *all* the lines of changing magnetism of the specimen. To correct for this, a specimen exactly similar to the one under investigation was wound with approximately the same number of turns as the induction helix J. This specimen was suspended in exactly the same position as that occupied by the other specimen during the actual experiment. A change-over switch allowed us to connect either the helix J and the coil F, or the above correction helix to a ballistic galvanometer. A variable resistance was included with this correction helix to equalise the total resistances of the two circuits, so that the galvanometer deflections obtained on reversing a heavy direct current in the magnetising helix were directly proportional to the induced electromotive forces. Let n and n_1 be the number of turns on the induction helix and correction helix respectively and θ and θ_1 the corresponding deflections produced by the reversal of a given current in H. Now the R amplitude actually neutralised corresponds to a change in magnetism of the specimen which is greater than that effective in producing the neutralising current in the coils B B. Hence the value U/M we obtain is greater than it would be if the total changing magnetism of the specimen were effective in producing current in B B, and the value should therefore be decreased in the ratio $n_1\theta/n\theta_1$.

But the coil F neutralised the induction in the helix J when the specimen was absent. It is therefore necessary that we use a similar small coil in series with the above correction helix to neutralise the induced current in the latter when no iron is present. A brass rod of the same dimensions as the specimen

and wound with a helix of the same number of turns as the correction helix, was put in series with a small coil and a ballistic galvanometer. This small coil was placed near the magnetising helix, and its position adjusted so that no deflection was observed when a heavy current was reversed in the latter. It was then fixed in position and in circuit with the correction helix when θ_1 was measured. It is probable, however, that this correction was small enough to be negligible.

Procedure.

The torsion head was placed in position and from it was suspended a long plumb-line which passed through the magnetising helix. The screws engaging the upper and lower flanges of the latter were adjusted until its axis coincided with the plumb-line. By means of the screws and springs in the flanges of the induction helix, it was made coaxial with the magnetising helix. The coils D and F were then arranged as previously described and the plumb-line removed.

The specimen was cut from a long wire which had been straightened by heating under tension, the length in all cases being 15·2 cm. A small loop of non-magnetic wire was soldered to each end of the specimen, the German-silver suspension was hooked into the upper loop, and the aluminium wire attached to the lower by an S-shaped hook. German-silver wire was used on account of its low damping factor for torsional oscillations; the suspensions used varying between Nos. 28 and 34 S.W.G., and of length about 35 cm. The aluminium wire was carefully straightened by rolling between heated metal plates; each end was slightly flattened and a small hole pierced with a needle near each extremity. One hole served for the insertion of the S hook, and the other for the attachment of the silk fibre which carried the weight W. The suspension was clamped in the torsion head, a heavy weight hung from the silk fibre and the suspension carefully heated. Shellac was placed around the loop junctions and melted several times whilst the system was thus under tension.

The specimen was then lowered into position and the torsion head rotated to bring the magnet needles parallel to the plane of the coils B B, which were then fixed as described under § 2.

An alternating current of about 1·2 amperes (R.M.S.) was passed through the magnetising helix, and the frequency adjusted until resonance was established; the vibrator was then regulated so as to obtain a stationary pattern on the stroboscopic disc. Throughout the experiment this frequency was maintained constant by the use of a double straight-wire rheostat in the

motor circuit. This type of resistance was used in order that it might be situated near the apparatus without producing any stray magnetic field.

The currents in the earth neutralising coils were next regulated until the resonance amplitude was a minimum, the coils B B being on open circuit. The rheostats were capable of very fine adjustment, and were placed some distance from the apparatus. The resonance amplitude for iron was usually between 1 and 2 cm. on the scale.

The coils B B were now switched in and the commutator so placed that the current in them was in the correct direction for reducing the resonance amplitude. The resistance S was first made very large, and then gradually reduced until the neutralisation value was approximately determined. From a curve plotted between the magnitude of the resonance amplitude and the corresponding values of S, the true value of the resistance necessary for complete neutralisation S_0 could be obtained. Later it was found that this neutralisation point was so sharply defined that it was unnecessary to plot this curve, and S_0 was taken as the average mean of a few pairs of resistances, usually differing by 100 to 200 ohms, which produced equal amplitudes on opposite sides of the neutralisation point. After switching off the A.C. in H we measured the steady deflection due to reversing a current of usually 200 milli-amperes in the coils B B. It was necessary to show that the permanent magnetism of the needles N remained constant under the experimental conditions. The steady deflections for known currents through B B were therefore observed before and after subjecting the needles to the effects of reversing much stronger currents in the circuit. These steady deflections showed that no appreciable change in the magnetic moment of the needles had taken place.

After rotating the specimen through 180 degrees about its axis, the above measurements were repeated and the scale distance measured. In early experiments the specimen was brought again to its initial position and the first measurements checked, but this was found to be unnecessary.

To obtain the torsion constant of the system, the weight W was detached and a cylindrical rod of known moment of inertia attached to the aluminium wire below the needles, a small hole being drilled through the centre of gravity so that the rod fitted well on the aluminium. The period was measured after replacing W, although the latter produced no apparent effect. The moment of inertia of the system was negligible compared with that of the added rod. The specimen was then removed and the correction for the current in J made as described in § 4.

It was essential to ascertain whether there was any mechanical vibration

of the oscillating system due to the alternator. The latter was mounted on a heavy wooden base which rested on solid rubber blocks, and driven at a speed to generate the same frequency as that natural to the system. No oscillation could be detected when a load, far in excess of that used in the determinations, was taken from the alternator.

Discussion of Results.

Table I.

No.	n.	S_0.	S_π.	S mean	$\phi \times 10^4$.	Correction factor.	C.	$K\left(=\frac{U}{M}\cdot\frac{e}{2m}\right)$.
1	42	3038	2888	2961	10·80	0·942	444·7	0·514
2	65	2800	3000	2897	6·06	0·942	767·5	0·508
3	—*	2850	3050	2946	6·12	0·942	767·5	0·505
4	60	2838	3238	3024	6·17	0·942	767·5	0·495
5	78	2858	3238	3037	5·78	0·942	828·2	0·500
6	31	3088	2638	2846	3·38	0·962	1310·0	0·504
7	31	3363	2888	3108	3·57	0·962	1310·0	0·487
8	36	2788	3738	3195	3·62	0·962	1374·0	0·504
9	37	3392	2799	3067	3·33	0·962	1432·0	0·503
10	37	2884	3529	3175	3·41	0·962	1434·0	0·498
11	43	4138	2388	3028	2·99	0·962	1555·0	0·496
12	—*	3088	3188	3137	3·15	0·962	1562·0	0·508
13	44	3888	2388	2959	2·95	0·962	1577·0	0·509
14	56	2888	3088	2985	2·18	0·962	2091·0	0·494
15	—*	2738	3138	2924	2·18	0·962	2095·0	0·506
16	56	2988	2888	2938	2·18	0·962	2135·0	0·513

* Frequency not recorded.

Iron.—The results of our experiments are given in Table I. Nos. 1 to 5 were with rods 1·65 mm. in diameter and the remainder 2·15 mm. The approximate frequency of the A.C. used in each experiment is found in the second column. S_0 and S_π give the neutralising resistances in ohms for the two positions of the specimen, the differences between them being due to those errors which appear to increase or decrease the R effect, according as the specimen is in the 0 or 180-degree position. By taking the harmonic mean of these experimental values we obtain the resistance given under "S mean." The following column gives the mean absolute deflection of the system in radians per ampere in the coils B B. The correcting factor follows in the seventh column, whilst that headed C gives the torsion constant of the suspension. The values of the R ratio $\frac{U}{M}$, divided by the theoretical value $\frac{2m}{e}$, are shown in the last column.

The value of the magnetising field was kept constant throughout the

determinations on iron, and was chosen so as to give saturation, *i.e.*, 90 Gauss.

It will be observed that the values approximate quite closely to 0·5, the mean value being 0·503 with an average variation of ± 0·006 from the mean. The value obtained for experiment 7 is inexplicably low, as the errors on the whole tend to increase the magnitude of the ratio.

Table II.

No.	n.	$H_{max.}$	S_0.	S_π.	S mean	$\phi \times 10^4$.	C.	Correction factor.	$K\left(=\frac{U}{M}\cdot\frac{e}{2m}\right)$.
1	38	90	2388	3788	2930	6·77	703·8	0·9226	0·505
2	40	45	2838	3038	2935	6·14	770·5	0·9226	0·501
3	42	140	2438	3588	2904	5·33	879·7	0·9226	0·501
4	43	75	2538	3538	2955	5·52	865·2	0·9226	0·502
5	44	176	2638	3038	2824	5·23	868·8	0·9226	0·500
6	50	113	2538	3538	2955	4·25	1107·0	0·9226	0·494

Nickel.—The results for specimens of nickel, diameter 1·65 mm., are given in Table II. In addition to the data given for iron is the maximum value of the alternating field, $H_{max.}$, in the magnetising helix during the experiment. In order to determine the ratio for varying fields, eight more layers, of the same spacing as the original winding, were wound on the helix. This was necessary because otherwise the heating effects of currents of more than 1·5 amperes would probably have caused the shellac joints to yield. It was found also that the alternator ran much more steadily on low currents.

The values of K obtained for varying magnetic fields, above and below the saturation value, show the constant proportionality between change of magnetic moment and the corresponding change of angular momentum.

Results 1, 3 and 6 were obtained with the same specimen, whilst different specimens of the same size were used in 2, 4 and 5. The values of the R amplitude varied between 5 and 10 mm., according to the magnetising field used, the scale distance being about 65 cm. as before.

It was found that for some unknown reason the disturbing effects were much less troublesome than in the case of iron.

The average value of the ratio, as obtained from Table II, is 0·501 ± 0·002.

Table III.

No.	n	S_0.	S_π.	S mean.	$\phi \times 10^4$.	C.	Correction factor.	$K\left(=\frac{U}{M}\cdot\frac{e}{2m}\right)$.
1	23	2488	3838	3019	8·710	529·6	0·960	0·494
2	24	2563	3438	2938	8·602	531·6	0·960	0·503
3	25	2088	4588	2871	8·445	533·9	0·960	0·507
4	27	2588	3488	2972	8·265	555·1	0·960	0·499
5	28	2563	3488	2955	8·212	558·0	0·960	0·501
6	34	3638	2488	2951	7·658	599·8	0·960	0·503
7	22	2188	3688	2747	10·230	420·4	0·959	0·505
8	28	2138	3738	2720	8·438	502·6	0·959	0·503
9	28	3838	2188	2787	8·485	507·7	0·959	0·499
10	40	2188	3788	2774	5·781	747·2	0·959	0·503
11	21	3188	2438	2762	11·210	385·4	0·945	0·497
12	24	2213	3638	2752	8·380	519·5	0·945	0·503
13	25	3538	2188	2703	8·103	528·9	0·945	0·504
14	29	3738	2188	2760	6·137	701·8	0·945	0·496

Heusler Alloys.—Table III gives the results obtained for three Heusler alloys, taken from different castings, the approximate composition being in each case 12 per cent. aluminium, 63 per cent. copper and 25 per cent. manganese.

The preparation of these in a suitable size presented some difficulty, particularly in view of their extremely hard and brittle nature.* The following method of casting, as advocated by McLennan,† was adopted. The copper, contained in a graphite crucible, was heated to a molten state in a blast furnace, after which the manganese was added. When this was melted, the aluminium was added, and after stirring well, the contents were poured into a mould 16 cm. in length and 8 mm. in diameter. The casting was ground on an emery wheel, extreme care being necessary in the final stages owing to the smallness of the diameter required.

Results 1 to 6 were obtained with a specimen of diameter 1·95 mm., which showed little hysteresis. This specimen had an induction of 3,600 for the field used in the experiments, *i.e.*, 176 Gauss. In the next four results a specimen of 1·65 mm. diameter was used, which showed more hysteresis than the former. The induction for a field of 176 Gauss was 3,000. Nos. 11 to 14 give data for the third specimen which had a diameter of 1·55 mm., its magnetic properties being very similar to specimen No. 1. Low frequencies were employed for these alloys, in order to obtain the maximum resonance

* Preliminary experiments were made with two specimens kindly presented by Sir Robert Hadfield, but, unfortunately, these were not sufficiently magnetic for quantitative work.

† McLennan and Wright, 'Phys. Rev.,' vol. 24, p. 276, 1907.

amplitude, this varying inversely as the frequency of oscillation. Further, preliminary tests showed that, owing to the time lag experienced by a specimen in attaining its magnetisation, the effective changing magnetism falls off with increasing frequency. The amplitudes of the R effects for the three Heusler alloys varied between 5 and 8 mm.

The average value of the ratio from Table III is $0 \cdot 501 \pm 0 \cdot 003$.

Summary.

A new method is described of determining the gyro-magnetic ratio, and results obtained with it are given.

As in the ordinary resonance method, the specimen, suspended vertically by a fine wire along the axis of a helix, is magnetised by an alternating current of the same frequency as the natural frequency of the system; but the resulting resonance amplitude is now reduced to zero by a series of impulses timed to oppose those due to the gyro-magnetic effect.

As no measurement of magnetic moment, frequency, or damping is involved, a considerable gain in precision is obtained. The method is independent of time-lag in magnetisation, and so can be applied to the Heusler alloys.

The following table contains the mean values of the ratio obtained for iron, nickel and Heusler alloys.

Table IV.

Metal.	K	K*
Iron	0·503	{0·507, 0·501, 0·500}
Nickel	0·501	0·505
Heusler alloys	0·501	...

The number is in every case 0·5 within the limits of experimental error, and corroboration is thus afforded of measurements of the ratio recently carried out in this University by an independent method, the results of which are given under K.*

We are greatly indebted to the Colston Research Society of the University of Bristol for a grant towards the expenses of the investigation. We also wish to express our grateful thanks to Professor Chattock for suggesting the work, and, further, for the continual kindness and valuable suggestions we have received from him during its progress.

* Chattock and Bates, *loc. cit.*

The Discontinuity of the Hydration Process.

By William A. Davis and J. Vargas Eyre.

(Communicated by Prof. H. E. Armstrong, F.R.S. Received June 8, 1923.)

At the Linen Industry Research Institute, Belfast, where the work to be described was undertaken, the study of the absorption of moisture by textile materials has naturally occupied attention. It is clear from an examination of the literature that, in the past, far greater attention has been paid to the development and application of technical methods of drying and of conditioning than to the study of the nature of the changes which are involved. Herzog* has recorded certain physical changes in textile materials during hydration, but interest has been focussed more particularly upon the question of the regain of moisture when equilibrium is attained on exposing materials in a humid atmosphere. Orme Masson and Richards† and Schloessing‡ have studied the behaviour of cotton and other textile materials from this point of view, and owing, no doubt, to the importance precise information of this kind has in its commercial application, considerable attention has been given to questions of this kind. It has been thought desirable to examine carefully, not only the conditions which determine the equilibrium between the humidity of the atmosphere and that of the substance, but also and more particularly the rate of attainment of such equilibrium, this being a matter of special interest in the Linen Industry. Apart from the work of B. A. Keen§ on the evaporation of water from soil no attempt appears to have been made to follow accurately the rate at which hydration changes of this kind proceed. Our early observations, which were made last year, showed very clearly that a characteristic feature of both hydration and dehydration changes of cellulosic materials is a discontinuity of the process, and evidence in support of this view seemed so convincing that we were led to ascertain whether such discontinuity were in any way characteristic of these materials. From this point of view, we have more recently made a study of the hydration of salts, choosing calcium sulphate as a sparingly soluble salt, copper sulphate as a freely soluble salt, and isinglass as a typical colloid characterised by the readiness with which it absorbs water and the peculiar manner in which it swells.

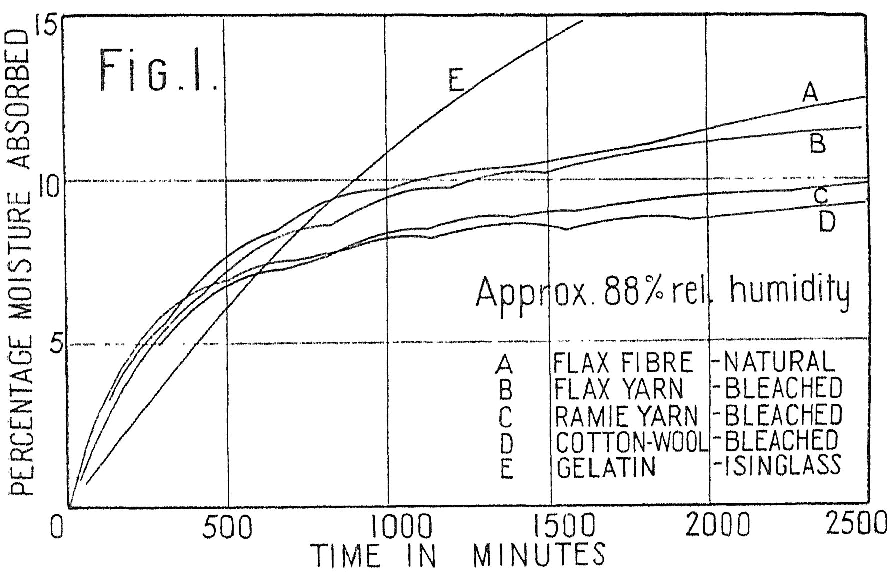
* 'Mitt. des Forschungs Instituts Sorau,' vol. I (1920).
† 'Roy. Soc. Proc.,' A, vol. 78, p. 412 (1907).
‡ 'Textile World Record,' vol. 36, p. 219 (1908).
§ 'J. Agric. Sci.,' vol. 6, p. 456 (1914).

The process of hydration has been studied in both directions. In many cases observations with a single substance have extended over several weeks, and when hydration was proceeding rapidly they were continued without interruption night and day, by working in shifts. It was found that the behaviour of substances generally, whether crystalline or amorphous, was similar in principle, and that hydration took place in a series of discontinuous steps, the change in rate occurring at frequent intervals. Moreover, action was found to occur along a series of simple curves, generally either parabolic or linear, which were of such a nature that the whole course of action, whether of hydration or dehydration, and covering either minutes, hours or days, could be accurately expressed by a series of simple equations in which time was reckoned from the original starting point.

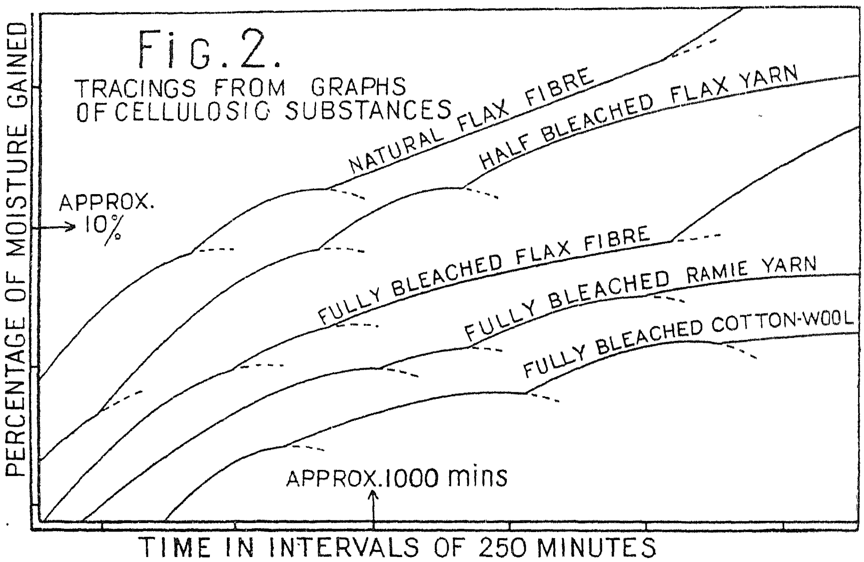
The results brought forward were so unexpected and difficult to understand that we feel it is desirable to place on record some of our observations in detail with an account of what appears to be the simplest manner of expressing the facts mathematically. The character of the discontinuity observed recalls the results obtained by Pickering in his study of the changes in the physical properties of aqueous solutions, although in these cases evidence of discontinuity was obtained by indirect methods.

Brief Account of Results.

In fig. 1 is given a set of graphs reduced from a series of carefully plotted curves showing the percentage of moisture taken up during definite periods of



time by various forms of cellulose. On such a scale, however, it is not possible to show clearly the character of the discontinuity we have observed. In fig. 2,

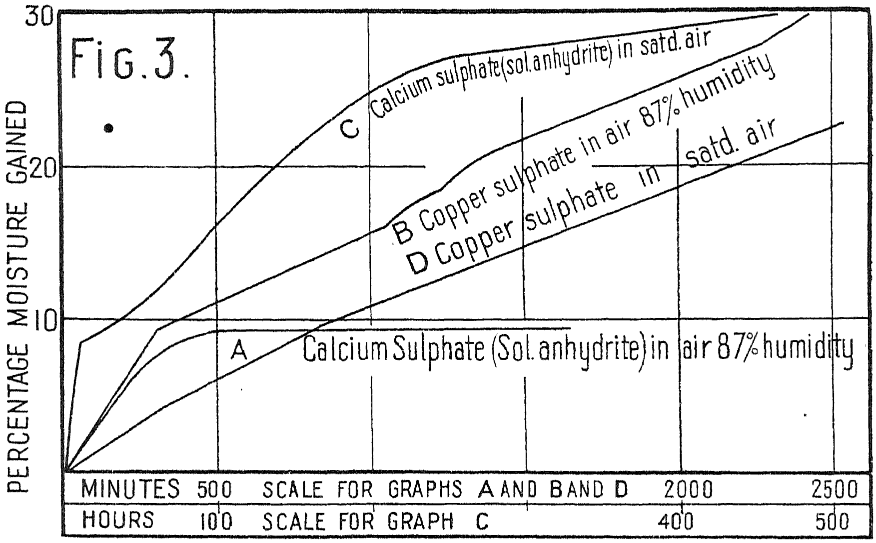


therefore, will be seen a set of tracings taken from corresponding regions of the original large scale curves. For convenience, these tracings are arranged in the order in which the substances attract moisture, and are, as closely as possible, correctly placed with regard to the percentage ordinate and time abscissa. As the zero, therefore, is not identical in all cases, these tracings must be regarded as diagrammatic, although the individual curves are all drawn to the same scale. They show a striking resemblance to one another, and, for the most part, are composed of a succession of parabolic sweeps with occasional straight portions.

The graphs in fig. 3 are those of salts (copper sulphate and calcium sulphate), and like those of fig. 1 show frequent discontinuity. With copper sulphate, the striking feature is that, instead of a succession of parabolic curves, the graph takes the form of a series of linear portions, with relatively very short parabolic sweeps. The hydration of calcium sulphate takes place very slowly in the later stages, and the segments form very long stretches extending over many hours, which enables the exact course to be minutely studied. For this reason this substance has been chosen as the basis of the mathematical treatment.

Attention must be drawn to the striking difference in the behaviour of the salts when exposed to air differing in humidity between 80 per cent. and 100 per cent. (the equilibrium point). It will be seen that calcium sulphate (soluble

anhydrite) is more rapidly hydrated at the equilibrium point, whereas copper sulphate shows the converse behaviour.



Up to the present, our observations with fibres have only been made at the lower humidity.

During the progress of hydration of the dry powdered salts, it has been observed that, at certain points, they show a marked tendency first to "ball" together and then, later, to "set" to a hard cake. The fact that such physical changes of state do not affect the course of hydration, and that the rate of action after such changes continues along paths similar to those previously taken is of considerable interest. Whether in form of powder or of hard cake the absorption of water seems to be regulated by precisely similar laws; when "set" the salt continues to gain in weight as though it were an open-mesh structure freely permeable to water vapour.

Experimental Methods.

The fibres and isinglass were at first dehydrated under reduced pressure, by heating about 1 grm. of the material, in a small glass weighing bottle, at 110° C., until constant in weight. The glass stoppers of the weighing bottles had sealed on to them a glass tube, bent at right angles, which was connected, through a large bottle containing phosphorus pentoxide, with a vacuum pump. Usually three or four specimens were dehydrated at the same time, each weighing bottle being directly connected with the drying vessel and heated in a Victor Meyer vapour bath containing boiling toluene. Dehydration was usually

complete in 1 hour, under a pressure of 12–15 mm. of mercury. The salts were generally heated at 150° or 200° C.

The dehydration of fibres and salts was also effected at the ordinary temperature over phosphorus pentoxide. This process, although slow and frequently occupying several weeks, has the advantage that it is not only possible to follow the dehydration throughout its whole course under constant conditions, but that it excludes all risk of change by heat. The same material can be used in successive experiments.

The dried substance, obtained by either method, was exposed to moist air of constant temperature and humidity and the gain of weight observed at frequent intervals. In all cases, a weighing bottle of similar size was used as a counterpoise and treated throughout in the same way.

The temperature of the vault in which the experiments were made was subject to only very slight and gradual variations even when the change of external conditions was considerable. The temperature was generally about 14° C. The humidity of the vault was about 86 per cent. "saturated," and did not fluctuate more than 2 or 3 per cent. during six months. A large covered glass tank, containing a few inches of water and covered inside with a wetted fabric, was used in studying hydration in "100 per cent. humidity," indicated by the identical readings of a wet and dry bulb thermometer within the chamber.

Weighings were made directly on an Oertling balance placed in the vault, the frequency of the weighings being determined by the rate at which change was proceeding. When the change was rapid, as at the beginning, weighings were made every 15 minutes, thus limiting the number of specimens forming a series to three, it being impossible to make accurate weighings more frequently than every 5 minutes. Later on (after 750 minutes), it was usually found sufficient to weigh every half hour, and later still every 2, 3, 6 or 12 hours.

Possible Variations of Hygrometric Conditions.

The relative humidity of the vault was determined from time to time by the dew point method and records of temperature and humidity (by wet and dry bulb thermometer) were made at every weighing; the variations have been considered in connection with the observed discontinuity. We have fully satisfied ourselves that no barometric change which has occurred during our experiments—although amounting in one case to a fall of 1·25 inches in 12 hours—has exercised a measurable influence on the rate of change. The extreme variation of temperature during the entire period of the observations

has not amounted to more than 0·5° C.; it has not been possible to correlate any discontinuity with the variations. The same is true of the change in humidity; this has not exceeded 3 per cent. during the whole period of any series, and the change has taken place very slowly, so that over long periods it was practically constant.

The most convincing proof that the observed breaches of continuity were not due to external conditions, but intrinsic, is found in the fact that, of four samples under observation at one time and behaving similarly, *one* only will suddenly change its velocity of hydration, to be followed, perhaps, after an interval by a change in velocity of one of the others, the remaining two continuing their course. Evidence of this individuality, and that the change issued from within and not from without, is given especially by the fact that large and sudden changes have occurred during periods of exceptional constancy of the external conditions. That the normal path of hydration is along a series either of parabolic or of linear curves is very clearly shown in experiments with soluble anhydrite and calcium sulphate hemi-hydrate, in which the temperature of the wet and dry-bulb thermometer remained unchanged and indicated 100 per cent. humidity throughout. Notwithstanding considerable variations of barometric pressure, the path of action was an unbroken parabola during 40 or 50 hours, and then changed to another parabolic curve, which in turn would continue unbroken during 50 to 100 hours.

Degree of Accuracy of the Observations.

The Oertling balance used was sensitive to 0·0001 grm., and the probable error of individual weighings less than 0·0002 grm., so that using 1 grm. of material the results were accurate to 0·02 per cent. Under our conditions of working, the same material, when weighed on 10 successive days, during which change was prevented, gave on eight occasions the same weight (within 0·0001 grm.); only on two days was a greater difference than this observed (and then less than 0·0002 grm.). Even in a saturated atmosphere, when a film of moisture forms on weighing bottle and counterpoise, the final weighings are constant to 0·0002 grm.

Discussion of Curves.

The outstanding feature of the graphs shown in figs. 2 and 3 is that each forms not a single continuous curve expressible by a single equation but a *composite* curve consisting of successive segments. Each of these segments, when analysed by the method developed below, consists generally of a single

parabolic curve of the type $x = Bt - Ct^2$, where x is the percentage of action (water lost or acquired) in time t reckoned from the start. In the linear segments, the constant C is zero. Sometimes the equation, especially at the beginning, may be the simple cubic $x = Bt - Ct^2 + Dt^3$.

In successive parabolic segments the constants B and C are related in a simple way and form a simple series; *it is a remarkable fact that practically all the successive parabolic segments pass through the origin of the co-ordinate system (a consequence of their being of the general form $x = Bt - Ct^2$), so that the progress of action from beginning to end can be accurately calculated (even during many days or weeks) in terms of time reckoned from the moment at which hydration started.*

As the general equation $x = Bt - Ct^2$ is of the same form as the simple equation of motion $x = v_0 t - \frac{1}{2}gt^2$ of a particle projected with an initial velocity V_0 and subject to a constant acceleration g, it is possible by treating the successive equations of hydration as equations of motion, accurately to follow the exact course of action and to calculate at every instant the progress (x), the instantaneous velocity ($\dot{x}$) and the acceleration ($\ddot{x}$) to which this is subjected, which is a measure of the force aiding or retarding hydration.

Thus the equation

$$x = Bt - Ct^2$$

gives by successive differentiation the equations

of velocity, $\dot{x} = B - 2Ct$

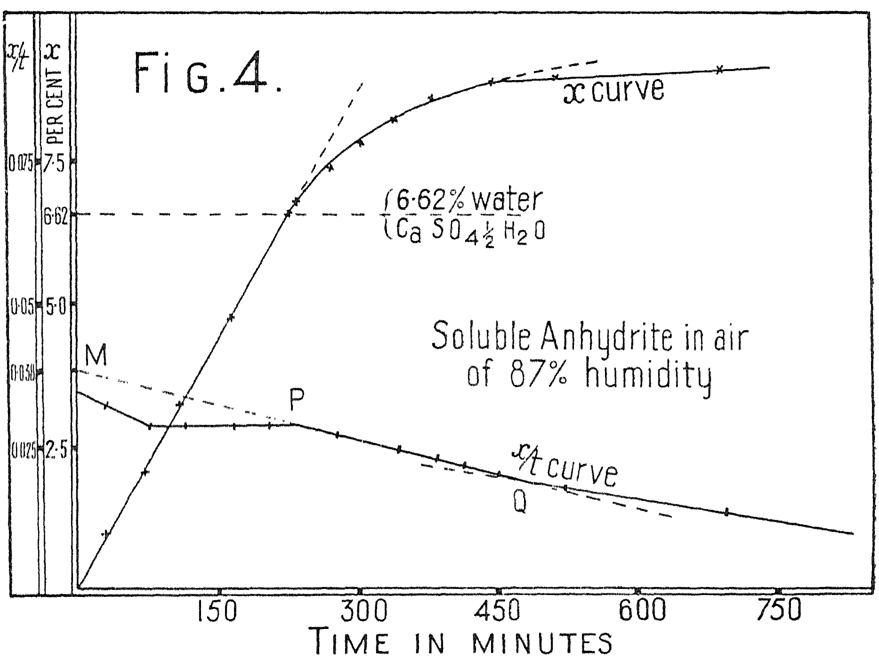
of acceleration, $\ddot{x} = -2C$.

Regarded in this way, each successive parabolic segment may be considered as representing a definite impulse, the measure of which is the initial velocity $V_0 = B$ (for $t = 0$) corresponding with the equation of that segment. This velocity decays during the parabolic path of progress, at a linear rate under the influence of the constant negative acceleration $-2C$, until it falls to zero at which instant the curve $x = Bt - Ct^2$ passes through a maximum. At this point (or very shortly afterwards) our observations show that the equation of action usually changes. Hydration which had completely ceased becomes renewed, as if with a fresh impulse, and proceeds along a new parabolic path. Over and over again with the same material this phenomenon has been observed to take place. Hydration after being brought practically to rest, begins again (although the external conditions remain constant) along a new parabolic path, only again to decay and again to be renewed. Hydration at last ceases altogether, the final impulses becoming smaller and smaller.

Illustrative Examples.

To illustrate the methods made use of in deriving the constants of the successive parabolic equations by simple graphical methods the following examples are given.

I. *Hydration of Soluble Anhydrite in Air of* 87 *per cent. Humidity.*—When soluble anhydrite prepared by completely dehydrating gypsum at a low temperature (110–150° C.) is exposed to moist air it at first takes up water at a practically constant velocity, action proceeding along a straight line,* until 6·62 per cent. has been acquired, corresponding with the formation of the hemi-hydrate, $CaSO_4, \frac{1}{2}H_2O$. Hydration in ordinarily moist air (60–80 per cent. humidity) does not stop here, a further quantity of water being taken up until the percentage gain may be 9 to 10 per cent. depending on the humidity. This second period of action takes place along a parabola, the velocity rapidly diminishing. Fig. 4 shows the graph obtained by plotting the values given in Table I.



Up to $t = 230$ minutes (Stage I) the velocity of hydration is practically constant, being 0·0288 per cent. water taken up per minute. Beyond

* *Cf.* W. A. Davis, 'Journ. Soc. Chem. Ind.,' vol. 26, p. 732 (1907).

Table I.—Hydration of Soluble Anhydrite

Stage and equations.	t mins.	Per cent. gain x (obs.)	x calc. from eqn.	Δ calc.-obs. per cent.	x/t obs.	x/t calc.
I. Linear:	30	0·96	0·86	−0·10	0·03200	
$x = 0·0288\,t$	70	2·04	2·02	−0·02	0·02914	
	112	3·25	3·22	−0·03	0·02893	
$\dot{x} = 0·0288$ (constant)	165	4·75	4·75	±0·00	0·02878	= average 0·0288
From						
$t = 30$ to	206	5·84	5·93	+0·09	0·02835	
$t = 230$	237	6·80	6·82	+0·02	0·02868	
$x = 1$ to 6·62 per cent.	275	7·39	7·92	−0·53	0·02687	
II Parabolic:	237	6·80	6·76	−0·04	0·02868	0·02852
$x = 0·038\,t—0·00004t^2$	275	7·39	7·43	+0·04	0·02687	0·02701
$\dot{x} = 0·038—0·00008t$	305	7·91	7·87	−0·04	0·02593	0·02580
$\ddot{x} = —0·00008$	340	8·27	8·29	+0·02	0·02432	0·02438
Range $t = 230$ to 480	380	8·72	8·66	−0·06	0·02294	0·02279
$x = 6·62$ to 9·025 p.c.	450	8·99	9·00	+0·01	0·01998	0·02000
	515	9·10	8·96	−0·14	0·01767	0·01740
	690	9·29	7·18	−2·11	0·01347	0·01041
III. Linear:	450	8·99	8·985	−0·005	0·01998	0·01996
$x = 8·4+0·0013t$	515	9·10	9·07	−0·03	0·01767	0·01761
$\dot{x} = 0·0013$	690	9·29	9·30	+0·01	0·01347	0·01348
Range from	1650	9·48	10·54	+1·06	0·00575	0·00639
$t = 480$ to $t = 681·8$						
$x = 9·025$ to 9·28 p.c.						
IV. Linear:	515	9·10	9·25	+0·15	0·01767	0·01796
$x = 9·15 + 0·0002\,t$	690	9·29	9·29	±0·00	0·01347	0·01347
$\dot{x} = 0·0002$						
From $t = 681·8$ to 1645	1650	9·48	9·48	±0·00	0·00575	0·00575
$x = 9·28$ to 9·48 p.c.	3030	9·49	9·76	+0·27	0·00313	0·00322
V.:						
$x = 9·466+0·000008t$	690	9·29	9·47	+0·18	0·01347	0·01372
$\dot{x} = 0·000008$	1650	9·48	9·473	−0·007	0·00575	0·00571
From						
$t = 1645$ to 3000	3030	9·49	9·490	±0·000	0·00313	0·00313
$x = 9·48$ to 9·49						

$t = 230$ (Stage II), when $x = 6·62$ per cent. (corresponding with $CaSO_4, \frac{1}{2}H_2O$) the equation of hydration changes to the parabola.

$$x = 0·038\,t - 0·00004\,t^2 \quad \text{(1)}$$

which gives by differentiation the equation of *velocity*,

$$\dot{x} = 0·038 - 0·00008t \quad \text{(2)}$$

and of *acceleration*

$$\ddot{x} = -0·00008 \quad \text{(3)}$$

in Air of 87 per cent. Humidity.

Δ	Hygrometry.			Velocities, etc.
	Dry bulb. °F.	Wet bulb. °F.	Humidity per cent.	
—	58½	56½	87·5	$x = 0 \cdot 032t$ gives 0·96 per cent.
—	58½	56½	87·5	v constant = 0·0288 per cent. per minute.
—	58½	56½	87·5	Intersects parabola II at t = 230 and x = 6·624.
—	58½	56½	87·5	
—	58½	56½	87·5	$CaSO_4$, $\frac{1}{2}H_2O$ = gain of 6·62 per cent.
—	58½	56½	87·5	
—	58½	56½	87·5	Equation ceases to apply.
−0·00016	58½	56½	87·5	V_0 = 0·038
+0·00014	58½	56½	87·5	V_{230} = 0·0196 x_{230} = 6·624 per cent. = $CaSO_4$, $\frac{1}{2}H_2O$
−0·00013	58¾	56¾	87·5	$V_{237 \cdot 5}$ = 0·0190 $x_{237 \cdot 5}$ = 6·77
+0·00006	59	57	87·7	V_{240} = 0·0188 x_{240} = 6·816
−0·00015	59	57	88·0	V_{400} = 0·0060 x_{400} = 8·800
+0·00002	59¼	56¾	85·0	V_{450} = 0·0020 x_{450} = 9·000
-0·00027	59	56½	84·7	V_{475} = 0·0000 x_{475} = 9·025
−0·00306	58½	56½	87·5	Equation ceases to apply after t = 475. (V changes at t = 230 from 0·0288 to 0·0196 = $\frac{2}{3}$ approx.; x = maximum at t = 475 x = 9·025 per cent.; V_{475} = 0·000.
−0·00002	59¼	56¾	85·0	Takes up at t = 480, intersection of II and III.
−0·00006	59	56½	84·7	V increases from 0·000 to 0·0013 per cent. per min.
+0·00001	58½	56½	87·5	V constant throughout = 0·0013 per cent. per min.
+0·00064	58½	56¼	86·0	Ceases to apply at 681·8 intersection with IV.
+0·00029	59	56½	84·7	Does not apply.
±0·0000	58½	56½	87·5	Velocity falls at t = 681·8 to 0·0002 per cent. = 1/6·5 that of Stage III.
±0·0000	58½	56¼	86·0	V constant = 0·0002
+0·00009	58¼	56	86·0	Ceases to apply after t = 1645.
+0·00025	58½	56½	87·5	Does not apply.
−0·00004	58½	56¼	86·0	At t =1645 V falls from 0·0002 to 0·000008.
+0·00000	58¼	56	86·0	No further increase during 10 days.

The hydration takes place as if due to an initial velocity at $t = 0$ of 0·038 per cent. per minute, which is subject to a constant negative acceleration, — 0·00008 per cent. per minute per minute.

At $t = 230$ minutes the intersection of the straight line $x = 0 \cdot 0288t$ with the parabola, the velocity calculated from equation (2) is $V_{230} = 0 \cdot 0196$, which is nearly half the velocity V_0 of the parabola ($t = 0$, $V = 0 \cdot 038$).

At $t = 237 \cdot 5$ minutes the velocity $V_{237 \cdot 5} = 0 \cdot 0190 = V_0/2$, whilst at

$t = 475$ minutes (double $237 \cdot 5$) the velocity $V_{475} = 0$. That is under the influence of the constant "drag" of $-0 \cdot 00008$ per cent. per minute per minute, the hydration has been altogether brought to rest. *Continuance beyond this point of the parabolic law of action would give a negative velocity of hydration, causing loss not gain of water.** *For hydration to continue beyond $t = 475$ minutes a change in the equation of action must necessarily occur.* Actually, shortly after this point (viz., at $t = 480$ mins.†) the equation expressing hydration becomes the linear (Stage III).

$$x = 8 \cdot 4 + 0 \cdot 0013t$$

which gives the velocity

$$\dot{x} = +0 \cdot 0013 \text{ constant.}$$

The velocity of hydration by this change of system is suddenly increased from 0 to $0 \cdot 0013$ per cent. per minute as if by a sudden impulse. From $t = 480$ minutes to $t = 681 \cdot 8$ ($x = 9 \cdot 025$ to $9 \cdot 28$ per cent.) the rate of hydration is constant with this value, but at $t = 681 \cdot 8$ minutes the velocity again undergoes change (Stage IV), this time suddenly falling to $0 \cdot 0002$ per cent. per minute, which is less than one-sixth its value just before. Hydration continues with this comparatively small velocity until $t = 1{,}645$ minutes, when another abrupt fall of velocity occurs to $0 \cdot 000008$ per cent. per minute (1/25 the velocity in Stage IV), which covers the interval (Stage V) $t = 1645$ to $t = 3000$ minutes, when hydration finally ceases.

From the above results it is clear that hydration in this case is brought to rest, not as the result of a steady and continuously acting force, but by a series of abrupt changes in the molecular mechanism, as a result of which the velocity of change becomes smaller and smaller.

The x/t Graph and the Method of Deriving the Equations of Hydration.—In the lower part of fig. 4 are plotted the values of the ratio x/t for the range $t = 0$ to $t = 750$. During the first four hours the rate of hydration is practically constant,‡ x/t having the value $0 \cdot 0288$ per cent. per minute. After $t = 230$ minutes, which corresponds exactly with the formation of $CaSO_4, \frac{1}{2}H_2O$ ($x = 6 \cdot 62$ per cent.), x/t begins to fall off regularly along a straight line, PQ

* On some few occasions a definite slight loss has indeed been observed.

† The point of intersection of the parabola $x = 0 \cdot 038t - 0.00004\ t^2$ with the straight line $x = 8 \cdot 4 + 0 \cdot 0013t$.

‡ During the addition of the first 1 per cent. of water the velocity is appreciably higher than this, x/t being $0 \cdot 032$. From 1 per cent. to $6 \cdot 8$ per cent. the velocity is, however, practically constant, with an average value $0 \cdot 0288$ per cent. per minute.

in fig. 4, which remains unbroken up to $t = 480$. During this period the change of x/t is expressed by the equation

$$x/t = 0 \cdot 0288 - 0 \cdot 00004\ (t - 230) \quad \ldots\ldots\ldots\ldots \quad (4)$$

Equation (4) is easily converted into the form

$$x/t = 0 \cdot 0380 - 0 \cdot 00004\ t$$

which gives $x = 0 \cdot 0380t - 0 \cdot 00004t^2$, in which time is reckoned from the start $t = 0$. This equation is of the general type $x = Bt - Ct^2$, and accurately expresses the course of action from $t = 230$ to $t = 450$, as shown by the calculated values in Table I, although not applicable before or afterwards.

The fact that the straight line *PQ*, representing the fall of x/t with time, can be produced to cut the axis of x/t gives a very simple graphical means of obtaining the constants B and C, characterising parabolic segments of the general type $x = Bt \pm Ct^2$. The x/t graph as a function of time often very clearly brings out the discontinuous character of the process and the points of transition, when the simple graph of x plotted against time does not do this. By the combined use of the x and the x/t graphs it is possible to derive in a very simple way the constants characterising the numerous changing systems which occur during a prolonged period of hydration, whether the equations are linear, quadratic or cubic. The following is an example of the method of using the x/t graph for evaluating B and C in a parabolic segment.

In fig. 4 beyond $t = 230$, x/t falls off as a simple linear function of time: $x/t = B - Ct$, reckoning time t from 0. When the straight line PQ in the graph, representing the rate of fall, is produced to cut the axis of x/t at M, it does so at a point which gives directly the value of x/t for $t = 0$, that is the value of B. In the case considered the value of B is read off directly as $0 \cdot 0380$. As the fall of x/t is continuous along the straight line MQ, from $t = 0$ to $t = 450$, the value of C at once follows. At $t = 0$, $x/t = 0 \cdot 0380$; at $t = 450$, $x/t = 0 \cdot 01998$; hence

$$C = \frac{0 \cdot 03800 - 0 \cdot 01998}{450} = 0 \cdot 000040.$$

The great advantage of the x/t graph is its linear character. The effect of plotting the x/t values is to introduce a new equation one degree lower. In the same way a cubic segment of the original hydration curve (x plotted against time) becomes a parabola in the x/t curve. The equation $x = Bt + Ct^2 + Dt^3$ gives $x/t = B + Ct + Dt^2$ a parabolic form from which B, C and D are easily derived. In this way the constants of a complicated series of hydration equations can readily be obtained.

II. Hydration of Soluble Anhydrite in Saturated Air at 57–58° F.—A second example chosen to illustrate the methods of working gives a case presenting slightly greater complications than the first. The values given in Table II were obtained in studying the hydration of soluble anhydrite in saturated air (100 per cent. humidity) up to the point of absorption of the first 9 per cent. It will be at once seen by comparing figs. 4 and 5 that in saturated air the course of hydration of soluble anhydrite is totally different from that occurring in air of 87 per cent. humidity.

In particular, there is no indication in the saturated atmosphere of the formation of the hemi-hydrate as a definite stage in the hydration. The point when $x = 6 \cdot 62$ per cent. is passed through on a continuous sweep of the curve. On the other hand, the initial rectilinear period instead of lasting up to $6 \cdot 62$ per cent. proceeds only as far as $5 \cdot 0$ per cent. ($2\frac{2}{3}$ hours) and then passes into a curved path covering 5 to $8 \cdot 2$ per cent. ($t = 2\frac{2}{3}$ to $t = 10$ hours). The apparently rectilinear portion from 0 to 5 per cent. is only very approximately represented by the equation $x = 2t$, and if the whole of the curve from 0 to 8 per cent. be regarded as a single curve it must be expressed as a cubic equation :

$$x = 2 \cdot 40\, t - 0 \cdot 24\, t^2 + 0 \cdot 008\, t^3 \qquad (5)$$

In Table II are given the values of x calculated from this equation, as well as the corresponding values of velocity ($\dot{x}$) and acceleration ($\ddot{x}$) for times from $t = 0$ to $t = 10$. The values of x calculated from the equation agree with those actually found, almost within the range of experimental error at times $t = \frac{1}{2}$, $1\frac{2}{3}$, 4 and $8 \cdot 48$ hours.

Reserving for a moment the discussion of the actually discontinuous nature of the rate of hydration, the peculiar properties of the cubic equation (5) will be dealt with.

As in the earlier equations expressing the hydration of soluble anhydrite in air of 87 per cent. humidity, the constants are remarkable, showing in particular the repetition of simple multiples of 2 and 3 such as 8 and 24, which occurred in the earlier series.*

* In the saturated air experiments time is reckoned in hours, whereas in air of 87 per cent. humidity it is reckoned in minutes. The velocity of $0 \cdot 0288$ per cent. per minute in the latter case becomes $1 \cdot 728$ per cent. per hour, that is exactly $0 \cdot 72$ times the initial velocity V_0 of the cubic equation ($2 \cdot 40$ per cent. per hour).

Table II.—Hydration of Soluble Anhydrite in Saturated Air at $57\frac{1}{2}°$ F. up to 8·89 per cent. addition of Water.

No.	t hours.	x gain of wt. per cent. (obs.).*	x/t (obs.).	x calc. from eqn. per cent.	Δ calc. obs. per cent.	Equations.	Calculated from equations. x per cent.	Velocity. $\dot{x}$	Acceleration $\ddot{x}$.
1	0	—	—	—	—		0	2·40	—0·48
2	$\frac{1}{2}$	1·126	2·252	1·141	+0·015	Equation . . . (5)	—	—	—
3	1	—	—	—	—	$x = 2·40\,t - 0·24\,t^2 + 0·008\,t^3$	2·168	1·944	—0·432
4	$1\frac{1}{6}$	2·33	2·000	2·486	+0·156		—	—	—
5	$1\frac{2}{3}$	3·34	2·004	3·370	+0·030	Velocity	—	—	—
6	2	—	—	—	—	$\dot{x} = 2·40 - 0·48\,t + 0·024\,t^2$	3·904	1·536	—0·384
7	$2\frac{1}{2}$	4·75	1·900	4·625	—0·125	—	—	—	—
8	3	—	—	—	—	Acceleration	5·256	1·176	—0·336
9	$3\frac{1}{3}$	5·72	1·716	5·630	—0·090	$\ddot{x} = -\ 0·48 + 0·048\,t$	—	—	—
10	4	6·31	1·578	6·272	—0·038	—	6·272	0·864	—0·288
11	5	6·91	1·382	7·000	+0·09	Accel. of acceleration	7·000	0·600	—0·240
12	6	—	—	—	—	$\dddot{x} = +\ 0·048$ (constant)	7·488	0·384	—0·192
13	$6\frac{2}{3}$	7·60	1·140	7·700	+0·10	—	—	—	—
14	7	—	—	—	—	*Note* :—	7·784	0·216	—0·144
15	8	—	—	—	—	x attains maximum at	7·936	0·096	—0·096
16	8·48	8·00	0·9434	7·97	—0·03	$t = 10$ hours.	—	—	—
17	9	—	—	—	—	$x_{10} = 8$ per cent. $\dot{x} = 0·000$. At $t = 5$ hours t term cancels 2·40 in $\dot{x}$ equation; $x = 7·00$ per cent. and $V_5 = 0·60 = \frac{1}{4}\,V_0$.	7·992	0·024	—0·048
18	10	8·20	0·8200	8·00	—0·20	Equation ceases to apply after 8 per cent.	8·000	0·000	0·000
19	$11\frac{2}{3}$	8·40	0·7200	8·03	—0·37		—	—	—
20	$18\frac{2}{3}$	8·89	0·4763	13·20	—4·31		—	—	—

* Throughout these observations the hygrometric conditions remained constant; wet bulb, 57·5° F.; dry bulb, 57·5° F.; humidity, 100 per cent.

By successive differentiations of equation (5) we have the equations of velocity and acceleration

$$\text{Velocity } \dot{x} = 2 \cdot 40 - 0 \cdot 48\, t + 0 \cdot 024\, t^2 \quad \ldots\ldots\ldots\ldots \quad (6)$$

$$\text{Acceleration } \ddot{x} = - 0 \cdot 48 + 0 \cdot 048\, t \quad \ldots\ldots\ldots\ldots \quad (7)$$

$$\text{Acceleration of acceleration } \dddot{x} = 0 \cdot 048 \text{ (constant)} \quad \ldots\ldots\ldots\ldots \quad (8)$$

If the action from $t = 0$ to $t = 10$ were strictly continuous it would be necessary to regard it as due to an initial velocity at $t = 0$ of $2 \cdot 40$ per cent. per hour, modified by forces causing a negative acceleration $\ddot{x}$, which is itself a linear function of time, having an initial value $\ddot{x}_0 = - 0 \cdot 48$ per hour per hour and decreasing with time under the influence of a constant acceleration of the acceleration, $\dddot{x} = + 0 \cdot 048$ per hour per hour per hour, which is exactly one-tenth of the initial value of $\ddot{x}$. In Table II are given the calculated values for $\dot{x}$ and $\ddot{x}$, showing the nature of their change from $t = 0$ to $t = 10$. At $t = 5$, when $x = 7 \cdot 00$ per cent., the velocity of hydration $\dot{x}$ has fallen to $0 \cdot 60$ ($\frac{1}{4}$ its value at $t = 0$), whilst the acceleration $\ddot{x}$ has fallen to $- 0 \cdot 240$, exactly half its value at $t = 0$. At $t = 10$ the value for x attains a maximum ($x = 8 \cdot 00$ per cent.)* and the velocity $\dot{x}$ and acceleration $\ddot{x}$ have both fallen to zero. Further continuance of the action beyond $t = 10$ would cause a loss of water.

Regarding equation (5) as a special case of the general equation $x = \mathrm{A} + \mathrm{B}t + \mathrm{C}t^2 + \mathrm{D}t^3$, we have the following remarkable values of the constants :

$$\mathrm{A} = 0$$

$$\mathrm{B} = 2 \cdot 40 = \frac{3 \times 2^3}{10}$$

$$\mathrm{C} = 0 \cdot 24 = \frac{\mathrm{B}}{10} = \frac{3 \times 2^3}{10^2}$$

$$\mathrm{D} = 0 \cdot 008 = \frac{\mathrm{B}}{300} = \frac{2^3}{10^3}$$

The expression for velocity $\dot{x}$ is such that when equated to 0, the condition for a maximum or a minimum, it gives only one value for t, viz., $t = 10$. It is a perfect square. At $t = 10$ both velocity and acceleration vanish.

The Actual Course of Hydration of Soluble Anhydrite from $t = 0$ to $t = 9$ hours.—Although the cubic equation (5) very approximately represents the course of hydration over the period $t = 0$ to $t = 9$ hours, and gives values at four

* Given by $dx/dt = 0$, that is when $0 \cdot 024\, t^2 - 0 \cdot 48\, t + 2 \cdot 40 = 0$. Solving for t we have $t = 10$.

points closely agreeing with those actually observed, it does not rigidly represent the hydration at intermediate times. Thus at $t = 2\frac{1}{2}$ hours the calculated value is lower by $0 \cdot 125$ per cent. than that actually observed whilst at $3\frac{1}{3}$ hours the difference is slightly less ($-0 \cdot 090$), at 4 hours again less ($-0 \cdot 038$), whilst at 5 hours and at $6\frac{2}{3}$ hours the difference becomes positive. These differences are far greater than can be possibly due to experimental error. Numerous examples of a similar kind have been observed.

An examination of the x/t graph in fig. 5 gives the explanation of the

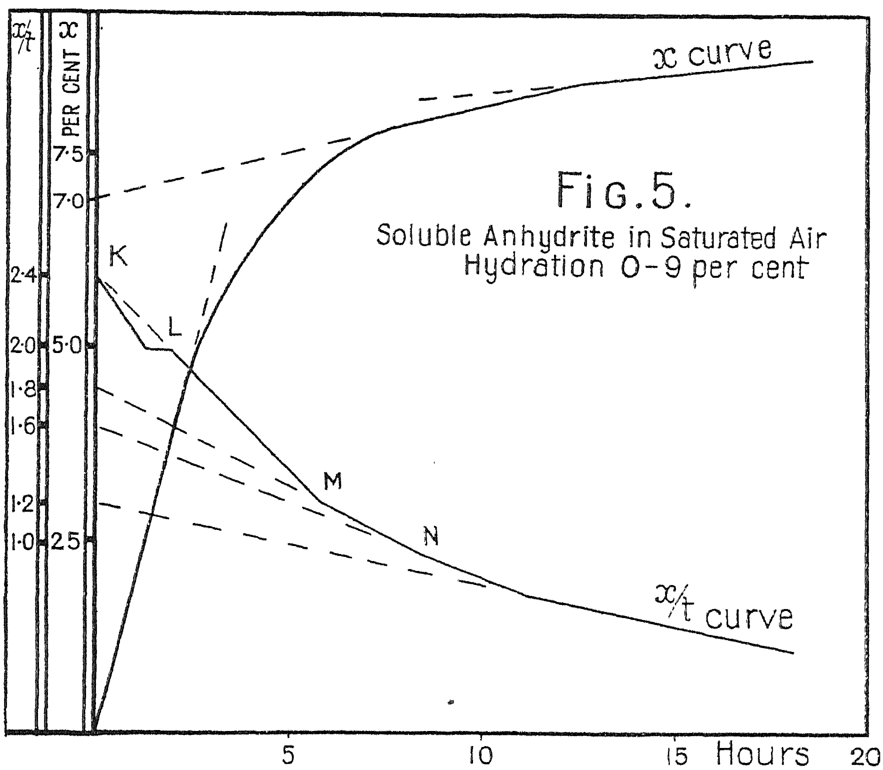


FIG. 5.
Soluble Anhydrite in Saturated Air
Hydration 0–9 per cent

phenomenon. Although the x graph might be taken as continuous, the x/t graph brings out its real discontinuous nature. Neglecting for a moment the period $t = 0$ to $t = 2$ hours, the x/t graph from $t = 2$ to $t = 6$ is a straight line LM, which cuts the x/t axis at K with x/t exactly $2 \cdot 40$.* At $t = 6$, the point at which change to another straight line MN occurs the value of

* For convenience of reference the values of x/t for $t = 0$ corresponding with the different straight line sections of the x/t graph may be called "basal" numbers.

$x/t = 1 \cdot 200$; that is, exactly half its value at $t = 0$. The equation for the straight line KLM of the x/t graph is therefore

$$x/t = 2 \cdot 40 - \frac{2 \cdot 40 - 1 \cdot 20}{6} = 2 \cdot 40 - 0 \cdot 200t \quad \ldots\ldots\ldots\ldots \quad (9)$$

and during the period $t = 2$ to $t = 6$ hours the parabolic equation expressing hydration is

$$x = 2 \cdot 40\, t - 0 \cdot 200 t^2 \quad \ldots\ldots\ldots\ldots \quad (10)$$

Beyond $t = 6$ the x/t graph changes to MN which cuts the zero axis at $1 \cdot 80$ (that is exactly two-thirds the value given by the first straight line). At $t = 9$, $x/t = 0 \cdot 90$ and the equation for the straight line is

$$x/t = 1 \cdot 80 - \frac{1 \cdot 80 - 0 \cdot 90}{9} = 1 \cdot 80 - 0 \cdot 100t \quad \ldots\ldots\ldots\ldots \quad (11)$$

The equation for the x curve (parabolic) over this period is

$$x = 1 \cdot 80t - 0 \cdot 100\, t^2 \quad \ldots\ldots\ldots\ldots \quad (12)$$

Beyond $t = 9$ the action slows down very greatly and changes its equation of action (*see* Table III).

Method of Deriving the Points of Change and the Magnitudes of Constants.

The equation (10) gives a maximum value for x when $t = 6$ hours. At this point the velocity of hydration has fallen to zero and beyond this point continuance of hydration according to the same equation would involve dehydration. At $t = 6 \cdot 00$, $x = 7 \cdot 20$ per cent., $x/t = 1 \cdot 200$. If change to another parabolic system occurs at $t = 6$, it is clear that at this point the value of x/t for both parabolas must be the same. If the equation of the new parabola be $x = B^1 t - C^1 t^2$, $x/t = B^1 - C^1 t$ and at $t = 6$, the point of change

$$1 \cdot 20 = B^1 - 6C' \quad \ldots\ldots\ldots\ldots \quad (13)$$

Now all parabolas of this type in the x graph, passing through $t = 6$, will be represented in the x/t graph by a series of straight lines passing through the point M in this graph.

These may be derived by imagining a straight line pivoted at M to revolve round this point so as to cut the axis x/t ; there will thus be an infinite number of such parabolas, the relative values of the constants B and C in the equation $x = Bt - Ct^2$ being determined for any one by the *direction* of the straight line ; that is, by the point at which it cuts the x/t axis. If, as appears from fig. 5, the equation which takes up action at $t = 6$ is represented by the line

Table III.—Equations showing the Course of Hydration of Soluble Anhydrite in Saturated Air.—[Dry Bulb Thermometer 57·5° F. Wet Bulb, 57·5° F. 100 per cent. Humidity Throughout.]

No.	Hours.	x per cent. obs.	Parabola Series. x calc. from eqn.	Parabola Series. Δ calc.-obs.	Parabola Series. Equation.	St. Line Series. x calc. from eqn.	St. Line Series. Δ calc. obs.	St. Line Series. Equation.	Stage and character.	x/t obs.
1	½	1·126	1·125	−0·001	$x = 2{\cdot}40t - 0{\cdot}30t^2$	—	—	—	I. Parabolic $x = 2{\cdot}40t - 0{\cdot}30t^2$	2·252
2	1⅙	2·33	—	—	—	2·333	+0·003	$x = 2{\cdot}0t$ (Nos. 2–3)	II. Linear $x = 2{\cdot}0t$	2·000
3	1⅔	3·34	—	—	—	3·333	−0·007			2·004
4	2½	4·75	4·75	±0·00	$x = 2{\cdot}40t - 0{\cdot}200t^2$	—	—	—	III. Parabolic $x = 2{\cdot}40t - 0{\cdot}200t^2$ Maximum at $t = 6{\cdot}0$	1·900
5	3⅓	5·72	5·72	±0·00	$x = 2{\cdot}40t - 0{\cdot}205t^2$ (Nos. 5–6)	—	—	—		1·716
6	4	6·31	6·32	+0·01		—	—	—		1·578
7	5	6·91	6·91	±0·00	$x = 2{\cdot}40t - 0{\cdot}2035t^2$	—	—	—		1·382
8	6⅔	7·60	7·60	±0·00	$x = 1{\cdot}80t - 0{\cdot}099t^2$	—	—	—	IV. Parabolic $x = 1{\cdot}80t - 0{\cdot}100t^2$ Maximum at $t = 9{\cdot}0$	1·140
9	8·48	8·00	8·00	±0·00	$x = 1{\cdot}80t - 0{\cdot}101t^2$	—	—	—		0·943
10	10·00	8·20	8·20	±0·00	$x = 1{\cdot}80t - 0{\cdot}098t^2$	8·20	±0·00	$x = 7{\cdot}00 + 0{\cdot}120t$	V. Linear. $x = 7{\cdot}00 + 0{\cdot}120t$	0·820
11	11⅔	8·40	—	—	$x = 1{\cdot}20t - 0{\cdot}288/7t^2$	8·40	±0·00	$x = 7{\cdot}00 + 0{\cdot}120t$		0·720
12	18⅔	8·89	8·89	±0·00	$x = 1{\cdot}20t - 0{\cdot}0388t^2$	8·876	−0·014	$x = 7{\cdot}80 + 0{\cdot}057\dot{7}t$ (Nos. 12–14)	VI. Linear $x = 7{\cdot}80 + 0{\cdot}057\dot{7}t$	0·476
13	30⅔	9·57	9·572	+0·002	$x = 0{\cdot}72t - 0{\cdot}0133t^2$	9·572	+0·002			0·3123
14	45⅔	10·44	10·450	+0·010	$x = 0{\cdot}48t - 0{\cdot}0055t^2$	10·438	−0·002			0·2286
14	45⅔	10·44	10·450	+0·010	$x=0{\cdot}48t-0{\cdot}0055t^2$	10·447	+0·007	$x = 5{\cdot}88 + 0{\cdot}10t$	VII. Practically linear, alternating between $x = 5{\cdot}88 + 0{\cdot}10t$ and $x = 5{\cdot}67 + 0{\cdot}10t$ Parabolic from 15 to 20 per cent. $x = 0{\cdot}20t - 0{\cdot}000425t^2$	0·2286
15	70	12·66	12·659	−0·001	$x=0{\cdot}32t-0{\cdot}001988t^2$	12·66	±0·00	$x = 5{\cdot}66 + 0{\cdot}10t$		0·1809
16	93	15·03	15·029	−0·001	$x=0{\cdot}24t-0{\cdot}000843t^2$	15·03	±0·00	$x = 5{\cdot}73 + 0{\cdot}10t$		0·1616
17	104⅙	16·30	16·300	±0·00	$x=0{\cdot}20t-0{\cdot}0004177t^2$	16·30	±0·00	$x = 5{\cdot}88 + 0{\cdot}10t$		0·1564
18	113½	17·23	17·229	−0·001	$x=0{\cdot}20t-0{\cdot}0004247t^2$	17·23	±0·00	$x = 5{\cdot}88 + 0{\cdot}10t$		0·1518
19	128½	18·53	18·53	±0·00	$x=0{\cdot}20t-0{\cdot}000434t^2$	18·52	−0·01	$x = 5{\cdot}67 + 0{\cdot}10t$		0·1442
20	140	19·67	19·67	±0·00	$x=0{\cdot}20t-0{\cdot}000425t^2$ $x=0{\cdot}18t-0{\cdot}000282t^2$	19·67	±0·00	$x = 5{\cdot}67 + 0{\cdot}10t$		0·1405

Table III—continued.

No.	Hours.	x per cent. obs.	Parabola Series.			St. Line Series.			Stage and character.	x/t obs.
			x calc. from eqn.	Δ calc.-obs.	Equation.	x calc. from eqn.	Δ calc.-obs.	Equation.		
21	153¼	20·86	20·859	−0·001	$x=0\cdot18t-0\cdot0002864t^2$	20·87	+0·01	$x = 5\cdot55 + 0\cdot10t$	VIII. Parabolic	0·13612
22	165¼	22·10	22·099	−0·001	$x=0\cdot18t-0\cdot0002800t^2$	22·10	±0·00	$x = 8\cdot88 + 0\cdot080t$	$x = 0\cdot18t - 0\cdot0002818t^2$	0·13375
23	174¼	22·74	22·742	+0·002	$x=0\cdot18t-0\cdot0002840t^2$	22·74	±0·00	$x = 8\cdot80 + 0\cdot080t$	Maximum $t = 319\cdot9$	0·13051
24	186	23·75	23·752	+0·002	$x=0\cdot18t-0\cdot0002812t^2$	23·76	+0·01	$x = 8\cdot88 + 0\cdot080t$	Linear from 20 to 22 per cent.	0·12769
25	198	24·73	24·730	±0·000	$x=0\cdot18t-0\cdot0002783t^2$	24·72	−0·01	$x = 8\cdot88 + 0\cdot080t$	$x = 5\cdot55 + 0\cdot10t$;.	0·12490
26	210	25·44	25·439	−0·001	$x=0\cdot18t-0\cdot0002803t^2$				Also linear from 22 to 25 per cent.;	0·12114
27	221½	26·06	26·059	−0·001	$x=0\cdot18t-0\cdot0002815t^2$				$x = 8\cdot88 + 0\cdot080t$	0·11765
26	210	25·44	25·44	±0·000	$x=0\cdot20t-0\cdot0003752t^2$				IX. Parabolic	0·12114
27	221½	26·06	26·06	±0·00	$x=0\cdot20t-0\cdot0003718t^2$				$x = 0\cdot20t - 0\cdot000372t^2$	0·11765
28	233·5	26·45	26·45	±0·00	$x=0\cdot20t-0\cdot0003713t^2$				Maximum at $t = 269\cdot5$ hrs.	0·11327
29	245	26·81	26·809	−0·001	$x=0\cdot20t-0\cdot0003697t^2$					0·10943
29	245	26·81	26·813	+0·003	$x=0\cdot18t-0\cdot000288t^2$	—	—	—	X. Parabolic	0·10943
30	258	27·16	27·163	+0·003	$x=0\cdot18t-0\cdot0002896t^2$	—	—	—	Average—	0·10527
31	269	27·42	27·420	±0·00	$x=0\cdot18t-0\cdot0002902t^2$	—	—	—	$x = 0\cdot18t - 0\cdot000290t$	0·10193
32	281	27·45	27·452	+0·002	$x=0\cdot18t-0\cdot0002929t^2$	—	—	—	Maximum at $t = 310$ hrs.	0·09769
33	293	27·66	27·663	+0·003	$x=0\cdot18t-0\cdot0002921t^2$	—	—	—		0·09440
34	306½	27·89	27·889	−0·001	$x=0\cdot18t-0\cdot0002904t^2$	—	—	—		0·09099
34	306½	27·89	27·890	±0·000	$x=0\cdot16t-0\cdot0002251t^2$	—	—	—	XI. Parabolic	0·09099
35	317½	28·14	28·139	−0·001	$x=0\cdot16t-0\cdot0002248t^2$	—	—	—	Average	0·08863
36	330½	28·28	28·282	+0·002	$x=0\cdot16t-0\cdot0002252t^2$	—	—	—	$x = 0\cdot16t - 0\cdot000225t^2$	0·08537
37	353½	28·51	28·506	−0·004	$x=0\cdot16t-0\cdot0002245t^2$	—	—	—	Maximum at $t = 355\cdot5$ hrs.	0·08065
37	353½	28·51	28·509	−0·001	$x=0\cdot14t-0\cdot0001679t^2$	—	—	—	XII. Parabolic	0·08065
38	388½	28·91	28·913	+0·003	$x=0\cdot14t-0\cdot0001688t^2$	—	—	—	Average	0·07441
39	412½	29·37	29·368	−0·002	$x=0\cdot14t-0\cdot0001668t^2$	—	—	—	$x = 0\cdot14 - 0\cdot000168t^2$	0·07120
									Maximum at $t = 416\cdot6$ hrs.	

MN in the x/t graph, which cuts the x/t axis at $1 \cdot 80$, we must have from equation (13)

$$1 \cdot 20 = 1 \cdot 80 - 6\, C^1 ; \text{ or } C^1 = 0 \cdot 100.$$

The value of the constant C^1, viz., $0 \cdot 100$, is therefore necessarily fixed by the "basal" number of the parabola; that is, by the value of B^1, the initial velocity at $t = 0$ corresponding with the equation. After $t = 6$, hydration is continued by the equation

$$x = 1 \cdot 80t - 0 \cdot 100t^2 \quad \ldots\ldots \quad (14)$$

This in turn can hold only for a limited period. At $t = 9$ it gives a maximum value of $x = 8 \cdot 1$, x/t being $0 \cdot 900$, and at this time the next change is due to occur. Change then takes place to a parabola with basal number $1 \cdot 6$, which from the value $x/t = 0 \cdot 900$ necessitates the equation

$$x = 1 \cdot 60\, t - 0 \cdot 0777t^2 \quad \ldots\ldots \quad (15)$$

which in turn has a maximum at $t = 10\frac{2}{7}$ hours.*

After the addition of 9 per cent. of water ($t = 21$ hours) the "basal numbers" of the equations rapidly fall and hydration progresses more and more slowly. Table III gives the results of observations up to 412 hours† with equations corresponding to the different phases of action.

The Simulation of Continuity by Actually Discontinuous Processes.

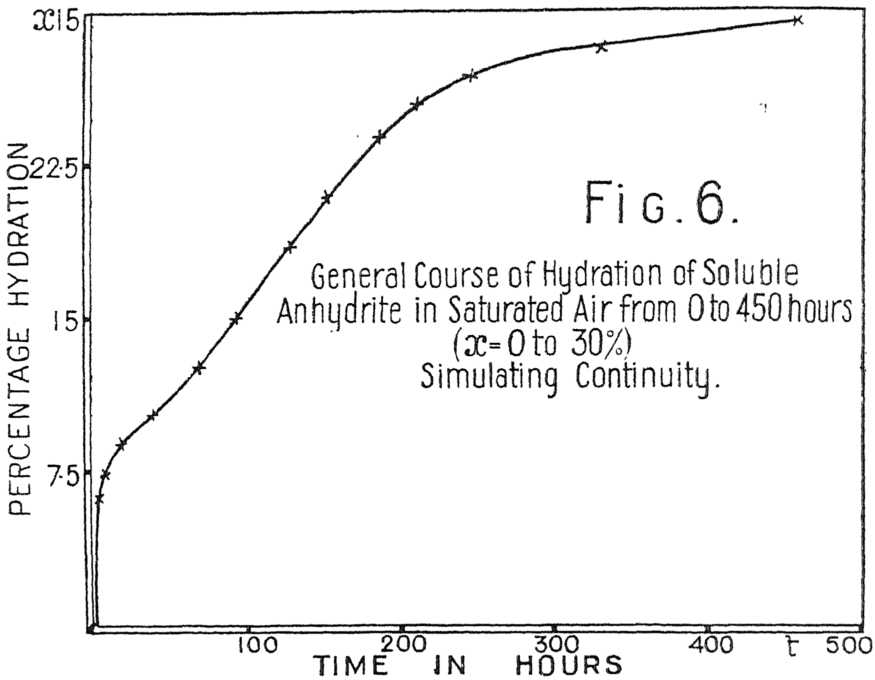
One of the most striking results of our method of making observations at very frequent intervals has been to show that although hydration actually proceeds along discontinuous paths, the average effect over considerable periods may closely simulate continuity. It is shown, for example, on p. 524 that whilst the actual course of hydration of soluble anhydrite in saturated air during the first 9 hours consists of three simple parabolic and 1 linear segment it corresponds at several points with the cubic equation $x = 2 \cdot 40t - 0 \cdot 24t^2 + 0 \cdot 008t^3$.

Fig. 6 shows the result of plotting only a few of the actual observations obtained during the hydration of soluble anhydrite in saturated air from $t = 0$ to $t = 450$ hours. From 8 per cent. onwards this curve presents the doubly-inflected appearance so frequently met with in cases of enzymic change, catalytic change and the phenomena of "auto-catalysis." There is a period

* The observed values from $t = 10$ to $11\frac{2}{3}$ are also on the straight line $x = 7 \cdot 00 + 0 \cdot 120t$ (*see* Table III).

† The hydration of soluble anhydrite in saturated air has been followed during 1,800 hours, that of the hemi-hydrate during 3 months, and that of copper sulphate for more than 3,000 hours.

of slightly increasing velocity (8 to 12 per cent.), followed by a long period during which action proceeds along a straight line with apparently nearly constant



velocity (12 to 24 per cent.), and a final period of decay in which the velocity falls (24 to 27 per cent.), and then proceeds very slowly along a straight line of very gentle slope.

Although this curve, plotted as in fig. 6 for the whole of its course, on a small scale appears to be practically continuous and with only a few observations would be taken to be so, its really discontinuous character is apparent when all the observations are plotted on a large scale in different sections; it is then clearly seen to consist of a series of parabolic or linear segments which can be rigidly expressed by the equations given in Table III. Only by neglecting whole series of intermediate values or by adopting unjustifiable methods of "smoothing" based on the assumption that the curves must necessarily be continuous can apparent continuity be obtained.

Further Consideration of Results.

On comparing the graphs representing our results, the striking similarity in the behaviour of all the substances examined will be obvious. Up to the present, we have not completed the mathematical treatment of the data

accumulated with reference to copper sulphate, isinglass and fibrous cellulosic materials, although complete records relating to the following series of observations are available.

Copper Sulphate.

Series I.—The material used in this work was that sold commercially as highly purified. The rate at which the dehydrated salt takes up water at 14° C. has been closely followed in an atmosphere of 87 per cent. relative humidity, during a period of 127 hours, involving 125 weighings. During this period, the weight increased by 55·73 per cent., no further change taking place up to 312 hours. The sample was then transferred to an atmosphere of 100 per cent. humidity, and observations continued during a total period of 3,108 hours. During this time, the gain in weight amounts to 77·64 per cent., and hydration is still proceeding at a slow rate. It should be observed that the percentage of water present in the usual pentahydrated salt is 56·44 per cent., and in the less usual heptahydrated salt 79·01 per cent.

Series II.—In this case the dehydrated material, as used in Series I, was weighed at intervals of 50 minutes during hydration in an atmosphere completely saturated with water, but at the same temperature (14° C.). Under these conditions, anhydrous copper sulphate takes up moisture at a far slower rate, fig. 3, than when exposed in the dryer atmosphere (87 per cent. relative humidity); only after the expiration of 7,200 minutes had this sample been hydrated to the same degree (55 per cent.) as the previous sample, exposed in 87 per cent. humid air, was during 6,200 minutes.

Series III.—In this series, discrimination was made in the size of the crystal particles previous to dehydration. Samples were separated, by sifting, into very fine, medium and coarse crystals; these were dehydrated by heat and then allowed to hydrate

(*a*) in an atmosphere only 87 per cent. humid, involving 109 observations (during a period of 9,200 minutes) and a gain in weight of 55·70 per cent.;

(*b*) the specimens were then transferred to a saturated atmosphere at the same temperature and 80 further observations were made during the remainder of the period of 1,374 hours.

Series IV.—In this series the crystals of copper sulphate were reduced from the penta- to the trihydrate by exposure over phosphoric anhydride used in such quantities as to maintain a dry atmosphere. Two specimens, one consisting of sifted coarse crystals, the other of sifted fine crystals, were

used. This experiment involved 108 weighings, over a period of 56 days. Very different curves of action have been obtained in these two cases, but the mathematical series have not yet been worked out.

Cellulosic Substances. Fibres.

During the earlier part of our work we were concerned mainly with good quality flax fibre, a form of impure cellulose which comes on the market for spinning and weaving into linen. It contains, in association with the cellulose, appreciable quantities of wax-like and pectous substances, which modify materially its behaviour under different conditions of moisture, from a study of which the present enquiry has developed. After combing down to a very fine condition, the rate of hydration of such flax has been followed in comparison with the same material after extraction with carbon tetrachloride to remove wax, and then with a solution of ammonium oxalate to remove some of the pectous substances. A similar comparison has been made with fully bleached and specially purified cotton-wool (Jeweller's Wool), also with yarns prepared from flax and from ramie, some of which were partially bleached and some fully bleached.

In all these cases, the rate of hydration of the dried materials in an atmosphere of approximately 88 per cent. relative humidity has been systematically followed, and in some cases similar observations have been made during desiccation over phosphoric anhydride. The study of the hydration of cellulosic substances in an atmosphere saturated with moisture is in progress, but has not yet proceeded far. The following table will suffice to show the scope and character of our observations with this class of material in moist air.

In figs. 1 and 2 are shown the x graphs of the substances used in Series III and IV; the discontinuous character of the hydration process is very pronounced and consequently the mathematical treatment of the results is more complicated than in the case of the salts we have examined. There is a remarkable similarity in their general behaviour, a fact which is clearly shown in fig. 2 and further exemplified by the close accordance of the results obtained in Series II and VII, in which the materials used, in comparison with cotton wool, were (*a*) natural flax fibre, (*b*) the same after extraction with carbon tetrachloride and (*c*) the same after a further extraction with a boiling aqueous solution of ammonium oxalate.

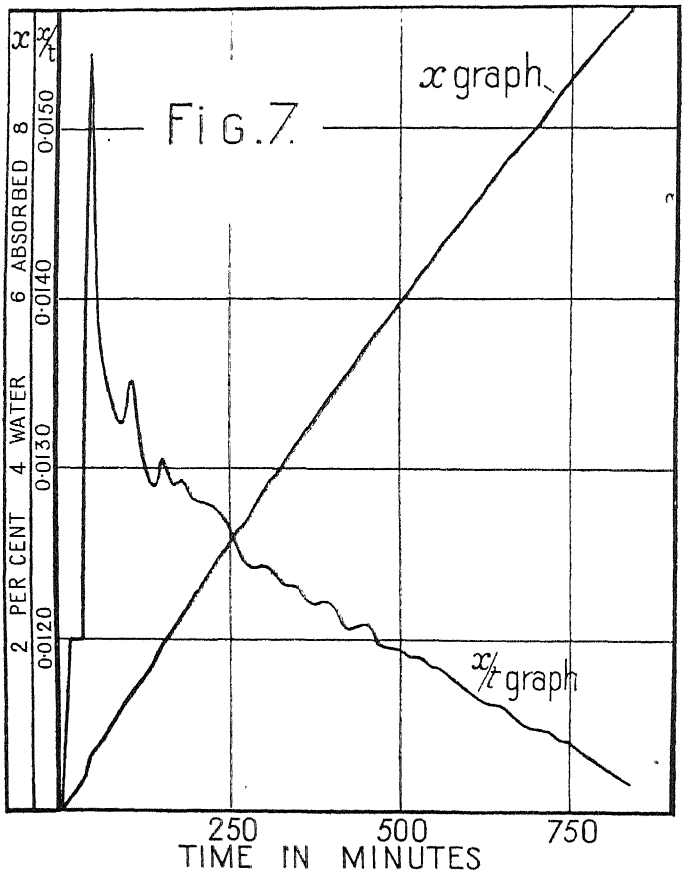
Generally, the rate of hydration of these cellulosic materials is comparable with that of calcium sulphate (soluble anhydrite) under similar conditions;

Series.	Materials.	Atmospheric conditions.	Period, hours.	Number of observations.
I.	Flax fibre (extracted) .... Flax yarn (bleached)	83 per cent. rel. humidity	238	27 27
II.	Flax fibre natural) .... ,, ,, (extracted) ,, ,, (extracted)	88 per cent. rel. humidity	424	76 76 76
III.	Flax fibre (natural) .... ,, ,, (bleached)	88 per cent. rel. humidity	555	74 74
IV.	Flax yarn (bleached) .... Ramie yarn (bleached) Cotton wool (bleached)	88 per cent. rel. humidity	247	60 60 60
V.	Flax fibre (natural) .... ,, ,, (extracted) Isinglass	89 per cent. rel. humidity	500	140 140 140
VI.	Flax fibre (natural) .... ,, ,, (extracted) ,, ,, (extracted) Cotton wool (bleached)	Over P_2O_5	10,573	45 45 45 45
VII.	Flax fibre (natural) .... ,, ,, (extracted) ,, ,, (extracted) Cotton wool (bleached)	82 per cent. rel. humidity	5,250	80 80 80 80

dehydration (Series VI), on exposure to the drying action of large proportions of phosphoric anhydride, proceeds at approximately two-thirds the rate at which the same materials are hydrated in an atmosphere of 82 per cent. relative humidity (Series VII). The character of their x graphs appears to be parabolic.

Gelatin.—As a typical example of a colloidal substance we have used ordinary gelatin (pharmaceutical isinglass) in hair-like form, without making any attempt to reduce it to the "isoelectric state." With this material we have completed a series of observations in an atmosphere of 89 per cent. relative humidity, extending over a period of 500 hours.

In the case of this substance, the rate of hydration appears to be continuous; but when the x/t graph is examined (fig. 7) there is striking evidence of an initial period of oscillation, the rate of hydration during the early period being subject to frequent variations.



Summary.

The curves obtained by following at short intervals the rate of hydration of widely different substances, including salts, gelatin and fibrous forms of cellulose, reveal a striking discontinuity of the hydration process.

Under the same conditions of relative humidity, the hydration curves for different substances are of a widely different character: the course of action, in the case of copper sulphate, being characterised by long linear portions and short parabolic sweeps; that of calcium sulphate by a predominance of parabolic portions of the path; cellulosic materials by the almost complete absence of linear portions of the hydration curve.

Substances exposed in an atmosphere saturated with water vapour (100 per cent. relative humidity) give an entirely different hydration curve from that obtained when the same substance is exposed in a drier atmosphere (88 per

cent. relative humidity); in some cases hydration may proceed at a slower rate, over a long period of time, in the atmosphere of greater humidity.

It has been observed that, notwithstanding the tendency of a powdery anhydrous salt to change its physical state by "setting" to a hard cake as hydration proceeds, the rate of hydration is not affected; the "set" mass continues to gain water as though it existed in the form of an open-mesh structure freely permeable to water vapour.

Note.—This work was practically complete when our attention was called on January 29th, 1923, to a communication by E. A. Fisher, entitled "Some Moisture Relations of Colloids," presented to the Royal Society, November 25, 1922, and published in their "Proceedings" on April 3, 1923. Mr. Fisher has studied the evaporation of water from natural wool when exposed to the drying influence of sulphuric acid in a confined space. His observations, therefore, are to some extent comparable with those obtained by us when using phosphoric anhydride; he has not, however, described any experiments on hydration similar to ours. His observations did not lead him to notice that the change is discontinuous, but he arrives at the conclusion that there is a change of rate by subjecting his curves to mathematical analysis. In this respect his conclusion is in agreement with ours, and his failure to obtain direct evidence may be attributed to the fact that his observations were not made at sufficiently frequent intervals.

Having regard to the technical importance of the problem under study and the advantageous conditions at our command, we propose continuing this inquiry and to extend it in a direction likely to afford an explanation of the peculiar character of hydration phenomena which our work has revealed.

The Behaviour of Metals Subjected to Repeated Stresses.

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(Both of The National Physical Laboratory.)

(Communicated by Sir Joseph Petavel, F.R.S. Received July 10, 1923.)

[Plates 27—31.]

Previous Work.

The essentially crystalline structure of metals has been definitely proved by many workers. Ewing and Rosenhain* showed that if a metal is permanently deformed by straining, its structure remains crystalline, plastic yielding being due to slipping along cleavage or gliding planes within the crystals, and, in the case of some metals, to the production of "twin" crystals. They failed to discover any signs of slipping when the applied stress was less than the primitive limit of elasticity of the material. These experiments were confined to static stresses.

As the result of some interesting experimental work, Beilby† advanced the theory that the process of "slip" involved a transition from the soft and crystalline phase to a hard and amorphous phase in the regions immediately adjacent to the plane of slipping, the term "amorphous" being used to indicate a state in which the molecular arrangement is haphazard in order and orientation as compared with that of the crystalline phase. The mobility of the amorphous phase involved during the process of slip is extremely transitory and the slip therefore is not reversible.

The effect of alternating stresses on the structure of metals was first studied by Ewing and Humfrey‡ employing reversed bending stresses. Under ranges of stress which produced failure they observed the growth of slip bands within the crystals. These slip bands increased in number and broadened out with reversals of stress. Failure was attributed to a process of attrition along the slip planes, resulting in a collection of débris which was squeezed out from the crystals. The crack thus formed spread from crystal to crystal, causing ultimate failure of the specimen.

* Ewing and Rosenhain, (*a*) 'Roy. Soc. Proc.,' vol. 65 (1899); (*b*) 'Phil. Trans.,' A, vol. 193 (1900).

† Beilby, 'Trans. Faraday Society' (June 9, 1904). 'Roy. Soc. Proc.,' A, vol. 79 (1907).

‡ Ewing and Humfrey, 'Phil. Trans.,' A, vol. 200 (1903).

If a ductile metal is strained beyond the yield-point and the load released, then, on re-straining immediately, the metal seems to be devoid of elasticity. In order to account for this fact, Rosenhain* has devised an important amendment to Beilby's amorphous theory. He considers that the process of slip produces a "temporary mobile phase" which requires time for "setting." Such a phase, therefore, permits of reversible strain if applied immediately, and leads to the conclusion that if a metal is subjected to such a range of stress as to initiate slip, a state of repeated slipping will result at each reversal of stress, and thus "the limiting stress at which slip ceases to occur within the metal is the 'safe range' for alternating stresses."†

A study of the failure of metals under alternating direct stresses was made by Stanton and Bairstow.‡ Microscopical observations were confined to specimens subjected to alternations of stress of such intensity as to produce failure. The mechanism of failure was shown to be that of the production of slip bands leading to the ultimate formation of cracks and was regarded by the experimenters as being in accordance with the theory of repeated slipping.

The above is a brief summary of the mechanism of fatigue as deduced from observations made using the microscope. It remains to consider relevant observations obtained using other instruments of precision. Bauschinger,§ as a result of many experiments, put forward the theory that failure, under repeated stresses, would not occur if an elastic state of the material was reached, due to the applied stresses. It is necessary to remark that the elastic limit acquired need not coincide with the primitive elastic limits of the materials. The truth of Bauschinger's hypothesis was substantially confirmed by Bairstow.|| In the latter work, it was conclusively shown that the attainment of the elastic state was in many cases preceded by considerable plastic strain. Such plastic strain could not have occurred without the formation of slip bands, but the process of slipping must, at some stage, have been arrested. Hankins¶ has shown that commercially pure nickel has a safe range of stress, under reversed direct and bending stresses, that considerably exceeds the range of its primitive static yield-points; also, that if a thermocouple be applied to a specimen subjected to a range of stress considerably less than the fatigue

* W. Rosenhain, 'Journal Iron and Steel Institute,' No. 2 (1906).

† W. Rosenhain, 'Introduction to Physical Metallurgy,' p. 254.

‡ Stanton and Bairstow, 'Proc. Inst. Civil Engrs.,' vol. 166 (1906).

§ J. Bauschinger, (*a*) 'Mittheilungen aus dem Mechanisch-technischen Laboratorium der k. Technischen Hochschule in München,' Heft 13, Heft 25.

|| L. Bairstow, 'Phil. Trans.,' A, vol. 210, 1910.

¶ G. A. Hankins, 'Reports and Memoranda, No. 789, Aeronautical Research Committee.'

range, large bursts of heat occur which rapidly die away. The existence of these heat bursts in nickel has been confirmed by Haigh, who has observed the same phenomenon in other metals. One of the present authors,* has demonstrated that copper, a metal which exhibits large plastic deformations at practically all stresses, has a very definite fatigue range.

Using a very delicate arrangement of thermionic valves, Desch† has detected permanent deformation in copper at a stress as low as 0·1 ton per sq. inch.

Present Research.

From a consideration of the experiments previously cited, the conclusion emerges that the appearance of slip bands is not, necessarily, any criterion that the applied range of stress is greater than the fatigue range of the material, which conclusion differs so essentially from previous theories as to warrant a further investigation. It appeared to the authors that some knowledge of the true mechanism of fatigue might be obtained if a material was used whose fatigue range, using reversed stresses, exceeded the range of the primitive yield stresses. With such a material a microscopical study of slip-bands in the "elastic" and "extra-elastic" ranges of stress would be possible. Preliminary experiments showed that "Armco Iron" was an almost ideal material for the purpose, and it has been selected for the present research. For the alternating stress experiments, it was decided to use a machine of the rotating beam type, and such a machine was adapted to permit of applying a simple bending moment over a considerable length of the specimen. Such an arrangement largely overcomes the effects of stress concentrations due to sudden changes of section at the point of maximum stress, while permitting a relatively large area to be explored microscopically. The phenomena of strain hysteresis under alternating stress and restitution of strain on removal of static tensile stresses seem to be so intimately connected with microscopical changes that mechanical tests bearing on these phenomena have also been carried out.

The main features of the research may be classified under the following heads :—

(1) Mechanical tests.

(2) A study of the Microstructure of the material when subjected to static tensile stresses.

(3) A study of the Microstructure of the material when subjected to reversed bending stresses.

* H. J. Gough, 'Engineering' (Sept. 8, 1922).

† C. H. Desch, 'Trans. Inst. Engrs. Shipbldrs. in Scotland,' vol. 25 (1922).

Material.

The Armco Iron was obtained from The Shelton Coal, Iron and Steel Co., Ltd., in the form of round bar of $1\frac{1}{8}$ inches diameter, and was used in the condition as received. A chemical analysis gave the following result.

	Per cent.
Carbon	0·012
Silicon	0·017
Sulphur	0·017
Phosphorus	0·014
Manganese	0·07

Mechanical Tests.

Tensile Test.

The tensile test was made using a 10-ton capacity single lever testing machine. In addition to obtaining the usual tensile properties, the test was so carried out as to study the behaviour of the material with regard to restitution of strain on removal of stress. An extensometer of the Martens type employing two rhombs with attached mirrors was used. Commencing with a stress of 0·4 ton per square inch, the stress was increased by regular increments of 0·2 ton per square inch. At each stress, extensometer readings were taken, the stress then being reduced to 0·4 ton per square inch, extensometer readings being again taken and the stress raised to the next higher value. As the influence of time was likely to be very important, the test was arranged so that each cycle of operations took 1 minute. The observed strains are plotted in fig. 1. It will be seen that a definite limit of proportionality was obtained at a stress of 9·85 tons per square inch, but at all loads a definite set was observed on reducing the applied stress. These "sets" are shown plotted, the strains being shown to a scale ten times greater than those in the accompanying stress-strain curve. The set increases with stress in a regular manner until at a stress of 9·4 tons per square inch, the rate of increase suddenly changes. At no stress, therefore, can the material be said to be perfectly elastic. It is probable that some of the observed set would disappear with time (elastic after-working).

Compression Test.—The compression test was carried out on a 50-ton single lever testing machine. Special axial loading shackles were employed to eliminate all bending stresses, the ends of the test piece being carefully ground. The mirror type of extensometer was again used. The resulting stress-strain

curve obtained is shown in fig. 1. It will be seen that, as in the tensile test, clearly defined limits of proportionality and yielding were obtained. The

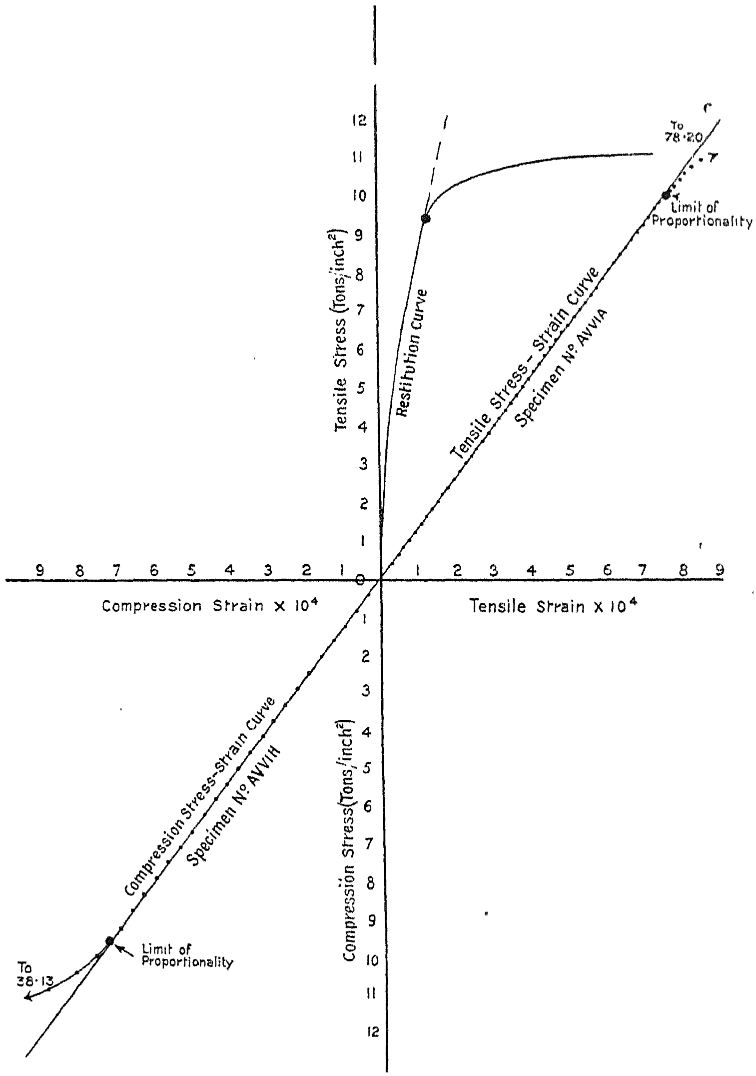


FIG. 1.—Mechanical Tests on Armco Iron.

numerical results of the static tensile and compression tests will be found in Table I.

No value could be obtained for the compressive ultimate stress as, owing to the extreme ductility of the material, the specimen deformed plastically under increasing loads. At a load of 100 tons the test was discontinued.

Table I.

	Tensile Test.	Compression Test.
N.P.L. No. of specimen	AVV1A	AVV1H
Diameter, inches	0·564	0·871
Area, sq. inches	0·2498	0·5985
Extensometer gauge length, inches	2·0	1·0
Length of specimen, inches	—	2·0
Stress at limit of proportionality, tons per sq. inch	9·85	9·65
Stress at yield point, tons per sq. inch	11·03	11·30
Ultimate stress, tons per sq. inch	20·9	—
Per cent. elongation at fracture	47·5	—
Per cent. contraction of area	66	—
Value of Young's modulus (E), lbs. per sq. inch $\times 10^{-6}$	29·3	29·4

Fatigue Tests.

(1) *Reversed Bending Stresses.*

The machine used is illustrated in fig. 2. The specimen is in the form of a rotating cantilever. Two methods of loading have been employed; single-point loading producing uniformly varying bending moment along the specimen, and two-point loading, producing uniform bending moment over a length of 3 inches. With the former arrangement, hollow and solid specimens have been employed; with the latter arrangement solid specimens only.

Determination of Fatigue Range on a Single Specimen using the Strain Method.

This method* may be briefly summarised as follows: A polished steel mirror is fixed to the free end of the specimen, and adjusted so that the plane of the mirror is at right angles to the axis of the specimen. With the specimen rotating at a constant speed equal increments of load are applied. At each load the slope of the mirror (and end of the specimen) is measured by a simple optical arrangement. Slope readings are plotted against applied load or maximum fibre stress to give load-slope or stress-slope diagrams. Usually, a straight line is obtained followed by a definite deviation from proportionality, the limit of proportionality being found to be in remarkable agreement with the fatigue limit or limiting stress.

* H. J. Gough, 'Engineer' (August 12, 1921); 'Engineering' (Sept. 8, 1922).

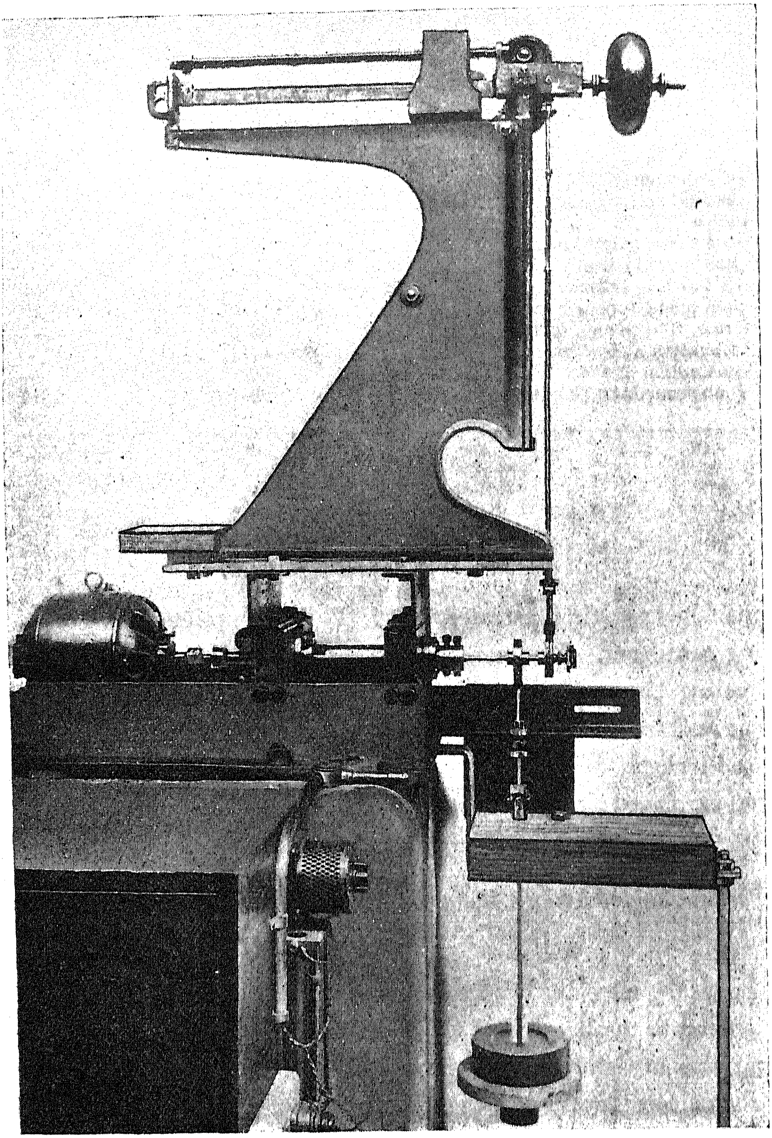


FIG. 2.

In the present tests, this method was employed for three types of specimen and two methods of loading.

(a) Solid specimens. Single-point loading.

(b) Hollow specimens. Single-point loading.

(c) Solid specimens. Two-point loading.

The values obtained for the fatigue ranges are shown in Table II.

Table II.

N.P.L. No. of specimen.	Dimension of section, inches.	Speed r.p.m.	Form of specimen.	Method of loading.	Fatigue Range Tons per sq. inch.
AVV2E	0·400 diameter	2200	Solid.	Single point.	±12·8
AVV2E	0·400 ,,	400	,,	,,	±12·8
AVV1F	0·400 ,, / 0·313 bore	2200	Hollow.	,,	±12·3
AVV3A	0·313 diameter.	2200	Solid.	Two point.	±12·5

The variations in the above values of the limiting range of stress may be ascribed to slight differences of material, but are much more likely to be due to the fact that readings were not taken at the same applied stresses for the three types of specimen, hence the observed difference may be ascribed partly to experimental errors.

The average value of these results is seen to be ± 12·5 tons per square inch, which, it will be seen, is in good agreement with the results of endurance tests.

Endurance Tests.

The results of the endurance tests carried out are given in Table III.

Table III.

N.P.L. No. of specimen.	Form of specimen.	Method of loading.	Applied range of stress, Tons/sq. inch.	Reversals $\times 10^{-6}$.
AVV1E	Hollow	Single point	±11·8	7·08 unbroken
AVV1D	,,	,,	±12·5	6·0 ,,
AVV1D	,,	,,	±12·83	1·13 broken
AVV1G	,,	,,	±13·17	0·39 ,,
AVV1E	,,	,,	±13·85	1·03 ,,
AVV2E	Solid	,,	±12·4	4·00 unbroken
AVV2D	,,	,,	±12·0	27·99 ,,
AVV2D	,,	,,	±15·3	0·44 broken
AVV3A	,,	Two point	±12·77	10·7 ,,
AVV3B	,,	,,	±12·18	39·94 unbroken
AVV3B	,,	,,	±13·65	1·11 broken
AVV3C	,,	,,	±13·05	3·02 ,,

Of the test results given in Table III, it may be remarked that only the tests on the hollow specimens were undertaken for the definite evaluation of the limiting range of stress by endurance tests. The other results were obtained

during tests made in connection with the study of the changes of microstructure, change of speed effect and hysteresis loops, to be described later. It will be seen, however, that all the tests are in good agreement and indicate a fatigue range for the material between the values of $\pm$ 12·5 and $\pm$ 12·8 tons per square inch. The tests made on the hollow specimens are also very important from another point of view. The static tensile and compression tests show that the range of static yield-stresses is 22·30 tons per square inch. The fatigue range under reversed bending stresses cannot possibly be less than 25 tons per square inch. The opinion has often been expressed that the fatigue range cannot exceed the range of the static yield-stresses, but that such a result might apparently be obtained with bending stresses, using a solid specimen, owing to a re-distribution of stress after the yield stress has been exceeded in the outside fibres. Such a re-distribution of stress in a solid specimen certainly seems probable. In the present tests on hollow specimens the thickness of the tube wall is only 0·044″, with an outside tube diameter of 0·400″, and such a re-distribution of stress as to reconcile the calculated limiting fibre stress of $\pm$ 12·6 tons per square inch with a range of yield stress of $\pm$ 11·5 tons per square inch seems outside the range of possibility.

It may be mentioned that, subsequent to the completion of the present tests, experiments on annealed Armco Iron subjected to reversals of direct stress, using a Haigh machine, have shown that the fatigue range for this material definitely exceeds the range of its primitive yield-stresses, and the same result has also been found with the same material subjected to reversed torsional stresses using the Stromeyer machine.

Armco Iron can, therefore, be definitely said to possess a fatigue range which exceeds the range of its static yield-stresses, and, therefore, has justified its selection as a material for the present research.

Hysteresis Loops under Reversed Bending Stresses.

To assist in the interpretation of the results of the study of the microstructure of the material, under ranges of stress inferior to and superior to the fatigue range, it seemed desirable to study the corresponding variation shown by hysteresis loops under similar ranges of stress. The extensometer used (although simple in form) was very accurate, an optical lever of 98 feet in length being employed. Considerations of space forbid all but a brief summary of the observations. Hysteresis loops were recorded after various numbers of reversals when the specimens were subjected to the following ranges of stress —

(*a*) Stress range $\pm$ 4·3 tons/sq. inch (less than the range of the static limits of proportionality).
(*b*) Stress range $\pm$ 6·4 tons/sq. inch. ditto. ditto.
(*c*) Stress range $\pm$ 8·5 tons/sq. inch ditto ditto.
(*d*) Stress range $\pm$ 11·9 tons/sq. inch (exceeding the range of the static yield stresses but less than the fatigue range).
(*e*) Stress range $\pm$ 15·3 tons/sq. inch (exceeding the fatigue range).

A brief summary of the observations is as follows :—

(*a*) *Stress Range* $\pm$ 4·36 *Tons/sq. inch.*

A definite loop of extremely small width was observed. After 180,000 reversals, no diminution of the width of the loop could be detected.

(*b*) & (*c*). *Stress Ranges of* $\pm$ 6·4 *and* $\pm$ 8·5 *Tons/sq. inch.*

Hysteresis loops were recorded at various stages during 220,000 reversals at $\pm$ 6·4 tons/sq. inch and 2,500,000 reversals at $\pm$ 8·5 tons/sq. inch. The loops in both cases were of small but very definite width, and showed a very slight tendency to diminish in width with reversals of stress.

(*d*) *Stress Range* $\pm$ 11·9 *Tons per sq. inch.*

The loop was observed to grow in width between the application of 2,200 and 6,790,000 reversals. It then maintained a constant width during the application of a further 21,200,000 reversals. In other words, the material has arrived at a cyclic state at some number of reversals less than 7,000,000, which state having been achieved, no further alteration in the cyclical permanent set was observed during the remainder of the test.

(*e*) *Stress Range* $\pm$ 15·3 *Tons per sq. inch.*

During the application of 24,000 reversals, the loop was observed steadily to increase in width. After a rest of 18 hours, followed by 12,000 reversals, the loop had slightly increased in size. The effect of the rest had either been negligible or had been discounted by the subsequent reversals of stress. Further runs of 11,300 and 100,000 reversals showed little change in the width of the loop. The cyclic strain appeared to have settled down to a practically constant value. A long rest of 72 hours, followed by 50,000 reversals, had a striking effect, the width of the loop being diminished 46 per cent. During the application of subsequent reversals of stress the loop rapidly increased in width, fracture of the specimen resulting after a further 250,000 reversals. The growth

of the area of the hysteresis loop may have been due to the material reverting to the approximately cyclic state in which it existed prior to the rest, or to the rapid increase of hysteresis which is well known to precede failure, or to a combination of both effects.

Microscopical Investigation.

Static Tensile Stresses.

For these tests a 10-ton single lever testing machine was used. The specimen consisted of a flat strip 0·5 inch wide and 0·25 inch thick, the length of the parallel portion being 3·0 inches. One of the flat faces was polished, and the structure was developed by etching. In carrying out the tests a stress was applied for a period of five minutes, and the specimen was then removed from the machine and examined. It was replaced, subjected to the next higher stress and again removed, and so on. It is considered that the conditions in a test piece of this kind closely approach those obtained with the standard round test piece, and confirmation of this fact is obtained by the breaking stress found for the flat test piece, which is 20·8 tons per square inch as compared with 20·9 tons in the case of the round test piece.

The material was examined after being subjected to the following stresses :—

(*a*) 7·96 tons per sq. inch (below the limit of proportionality).

(*b*) 10·2 tons per sq. inch (above the limit of proportionality, but below the yield stress).

(*c*) 11·79 tons per sq. inch (above the yield stress, but below the limiting fatigue stress).

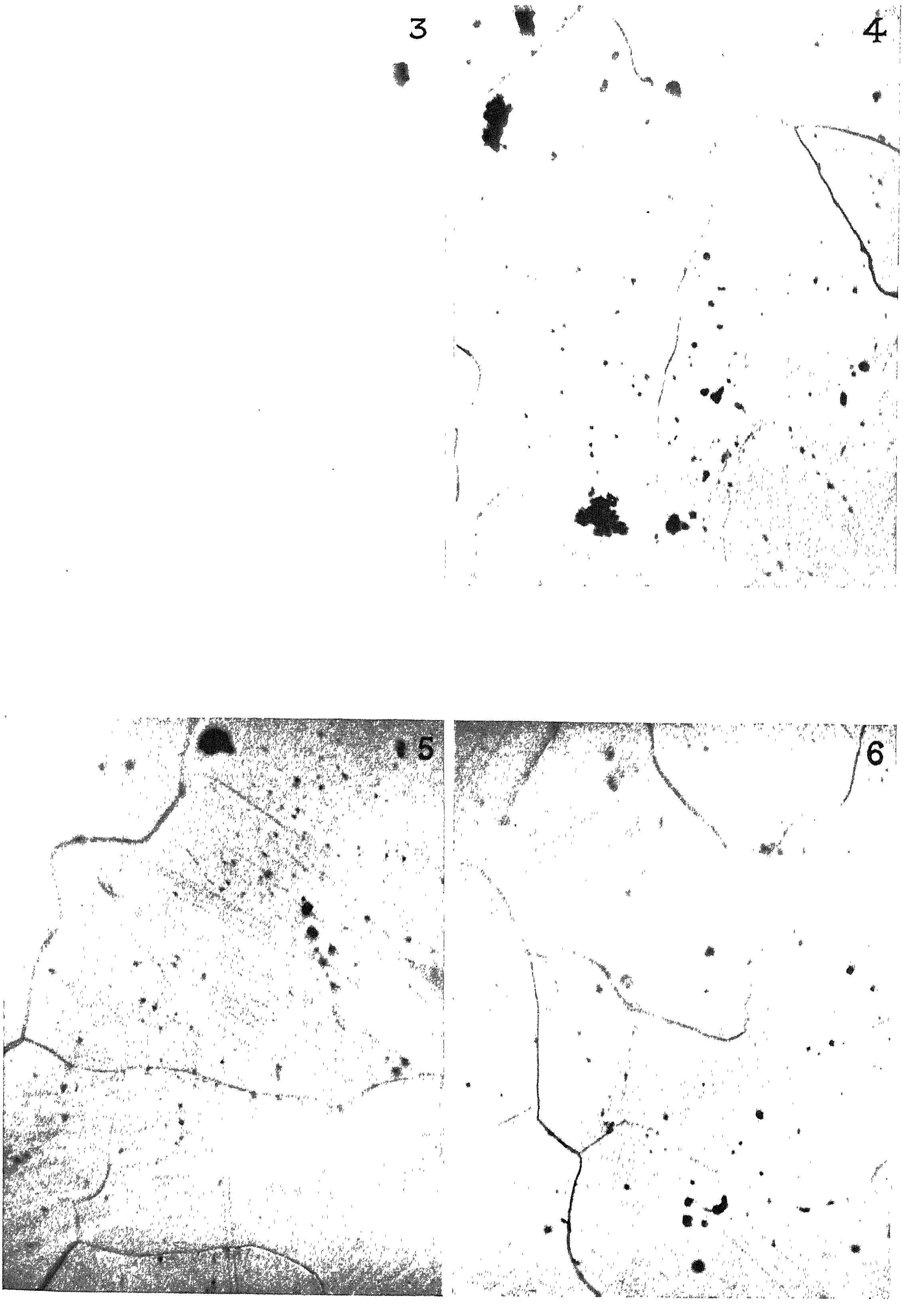
(*d*) 13·4 tons per sq. inch (above the fatigue limit, but below the breaking stress).

Fig. 3, Plate 27, shows the microstructure of the unstrained iron ; after subjecting the material to a stress of 7·96 tons per square inch, that is, below the limit of proportionality, no difference was observed.*

Fig. 4 shows the appearance of the material after the application of a stress of 10·2 tons per square inch, a stress intermediate between the limit of proportionality and the yield-stress. Very definite surface markings are now present ; they must be taken as indicating definite plastic strain, caused by the applied stress. In appearance they are similar to the slip bands normally obtained by stressing above the yield-point, and are probably similar in character.

Fig. 5 shows the appearance after the application of a stress of 11·79 tons

* All microphotographs are × 1400 ; except fig. 14, × 150.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per square inch, that is a stress greater than the yield-stress, but less than the fatigue range. The photograph shows the characteristic slip-bands of soft iron. Fig. 6, which represents the appearance after the application of a stress greater than the fatigue range, is not essentially different from fig. 5, and indicates a change in degree but not in character of the deformation.

In these tests no definite signs of permanent deformation of the material were observed after the application of stresses less than the limit of proportionality; definite signs of permanent deformation were found when the applied stress exceeded the limit of proportionality, but was less than the yield-stress.

Alternating Stresses.

The machine used in these experiments is shown in the photograph, fig. 2. Two-point loading was used giving simple bending over a length of 3 inches The specimens were of the solid type; a small flat, approximately 1 inch × 1/10 inch, was prepared on that portion subjected to uniform bending. This flat was carefully polished and etched in order to reveal the crystal structure. The specimen was placed in the machine and submitted to various ranges of stress; it was removed from time to time, examined and photographed. The effect of the flat on the strength of the section was extremely small.

In a preliminary experiment, a microscope was fitted to the machine in order that the microstructure could be examined without removing the specimen. In two further experiments, during which most of the photomicrographs accompanying this paper have been taken, the specimen was removed from the machine at intervals during the test, and examined by means of a microscope more suitable for high magnifications, and for more completely exploring the surface of the specimen. It was considered useless to study any one spot, since it was impossible to predict in what portion of the specimen first signs of yield would occur; a series of representative photographs has therefore been taken illustrating the structures found after the different treatments. In one case, however, three photographs of the same spot have been taken at different stages during an experiment.

The results of experiments on the three specimens amply confirm one another, and it is not considered necessary to describe those three experiments separately. The photomicrographs indicate the features characteristic of all the specimens.

Failure in each case ultimately occurred close to the centre of the portion of the section containing the flat, well removed from all fillets and changes of section. In addition, the number of reversals required to produce fracture,

and the corresponding stresses, are in very good agreement with other endurance tests previously quoted, showing that the stress calculation in the specimens here described is substantially correct.

The microstructure of the material has been studied after the application of varying numbers of repetitions of the following ranges of stress :—

(a) Less than the range of the static limits of proportionality.

(b) Exceeding this range, but less than the range of the static yield stresses.

(c) Exceeding the range of the static yield stresses, but less than the fatigue range.

(d) Exceeding the fatigue range.

(a) Structure of the Iron under a Range of Stress Less than the Range of the Static Limits of Proportionality.

Slight signs of deformation were observed after the application of 11,751,400 reversals of a range of stress $\pm$ 9·5 tons per square inch. Fig. 7 (Plate 28) shows definite signs of strain, consisting of faint surface markings visible in a few places only in the photograph, which have the appearance of very faint slip-bands within the crystals.

Markings of this kind were only found on a few crystals, and most of the crystals were quite clear. These marks are very infrequent and indistinct, and marks of a somewhat similar character were occasionally observed on unstrained specimens, but the authors think that the numbers of such marks increased considerably as a result of the application of the stress. Similar markings were found in a test piece subjected to a static stress less than the limit of proportionality.

(b) Structure after Subjecting to a Range of Stress Exceeding the Range of the Static Limits of Proportionality, but Less than the Range of Static Yield Stresses.

The effect of slightly increasing the range of stress so that it exceeds the range of the static limits of proportionality is to produce further signs of strain, of the same character as that already described. After this treatment most of the crystals were still free from signs of strain, but more were now found to be affected than in the previous case. The strain markings observed look like isolated slip-bands, which do not as a rule start from a crystal boundary, accompanied by a general roughening of the surrounding surface. The whole of the polished surface was carefully examined in order to determine

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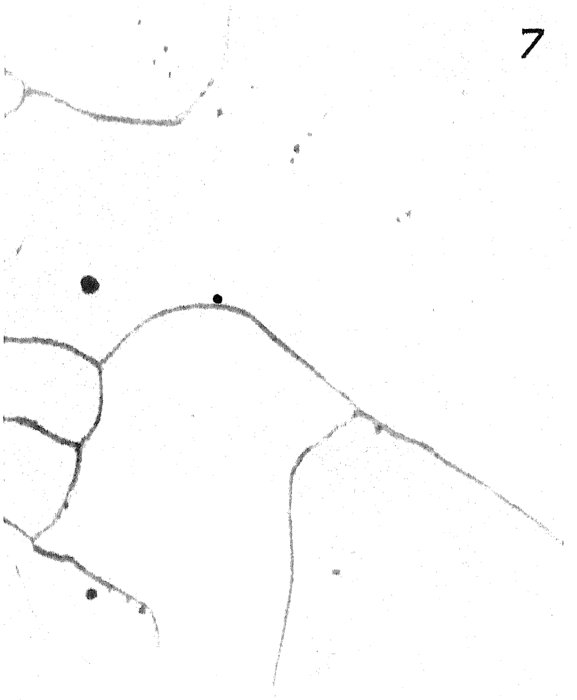

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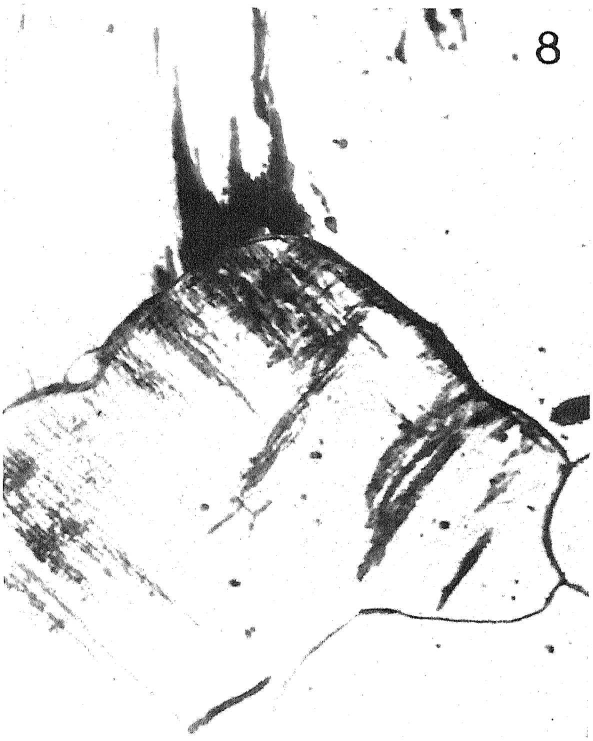

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if any "massing" of slip-bands could be observed, but this was found only in one spot.

(*c*) *Structure after the application of a Range of Stress, Exceeding that of the Static Yield Stresses but Less than the Fatigue Range.*

Under alternations of stress exceeding the range of the static yield-stresses, the appearance of the polished surface is very different from that typical of lower stresses. In certain of the crystals, areas are found that appear dark under low powers of the microscope, but when examined under high powers are found to consist of a series of roughly parallel markings that appear to be identical with slip-bands. Such markings are indicated in fig. 8, which represents a specimen that has been subjected to 300,000 reversals of a range of stress of $\pm$ 12·3 tons per square inch. The slip-bands in this photograph run in two directions approximately at right angles, but no one set of slip-bands runs right across the section of the crystal. The area in which visible slip has occurred is very irregular in shape, and bears no apparent relation to the shape of the section of the crystal. The broad dark bands, which represent aggregations of slip-bands, run in different directions in different crystals, and change direction at a crystal boundary.

Fig. 9 is a photograph from another specimen that has been subjected to 40 million reversals of a range of stress of $\pm$ 12·2 tons per square inch. The black masses of slip-bands are very pronounced and the variation of the direction of slipping from crystal to crystal is clearly shown. In nearly every case, the slip-bands appear to stop short of the crystal boundaries, which are clearly defined; this is quite a common but not a universal feature in this specimen. Particular attention is drawn to the fact that this specimen withstood 40 million reversals of the range of stress, which was 0·4 tons per square inch less than the previously determined fatigue range; there can, therefore, be little doubt that the fatigue range was not exceeded, and that the specimen would have withstood an indefinite number of reversals of this stress without breaking.

(*d*) *Structure after the Application of a Range of Stress Exceeding the Fatigue Range.*

The microscopical appearance of the surface of the specimen after raising the range of stress above the fatigue range is very similar to that of specimens stressed just below this range, except that the dark areas in which slip within the crystals has taken place are rather larger and more numerous; they do

not, however, appear to be essentially different. The comparison between the markings produced by stressing below and above the fatigue range is illustrated in figs. 10, 11 and 12 (Plates 29, 30), which represent the same spot after stressing as follows :—

Fig. 10. 40,000,000 reversals of $\pm$ 12·2 tons per square inch, that is, above the range of the static yield-stresses, but below the fatigue range.

Fig. 11. A further 100,000 reversals of $\pm$ 13·6 tons per square inch (above the fatigue range).

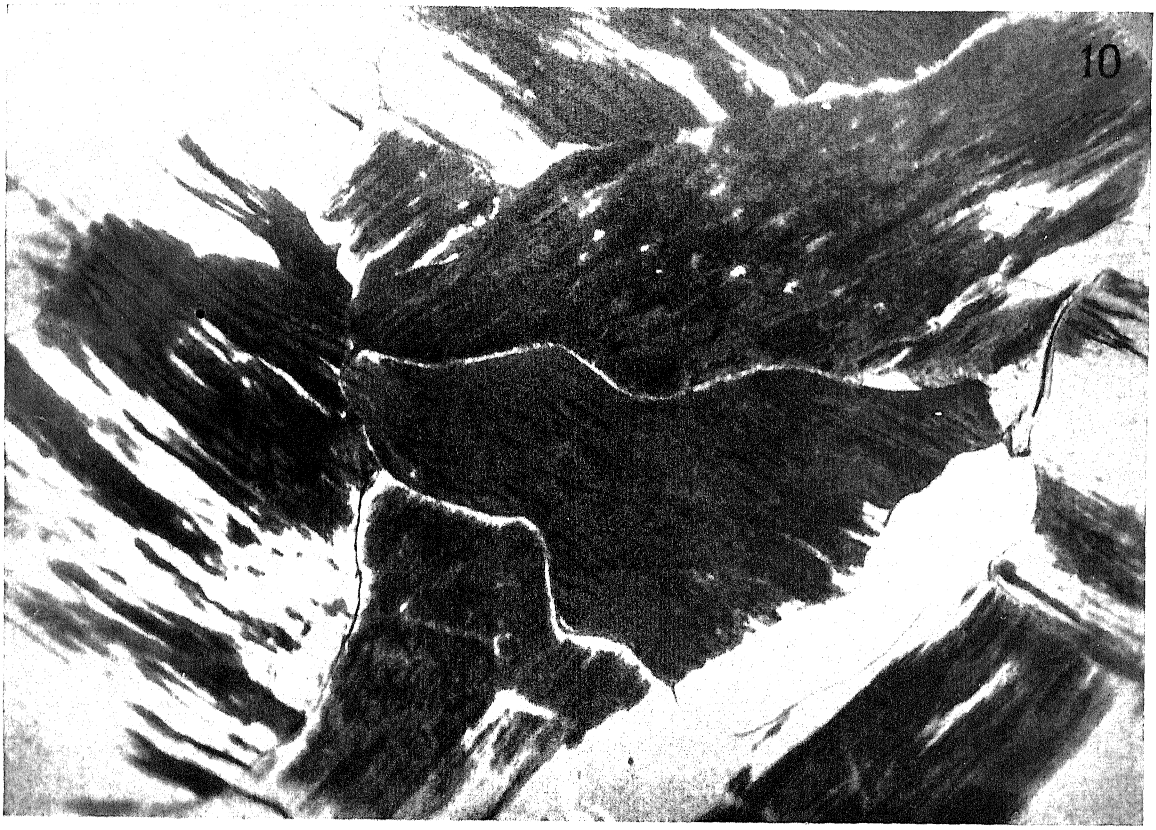
Fig. 12. A further 1,018,200 reversals of $\pm$ 13·6 tons per square inch, after which the specimen fractured. The spot photographed is very close to the fracture (about 0·04 inch), and is shown under a lower magnification in fig. 13 (Plate 30).

Fig. 10 shows a profusion of fine dark slip-bands which constitute the dark area formed by 40 million reversals of a range of stress a little below the fatigue limit. Fig. 11 shows that 100,000 further reversals of a range of stress of $\pm$ 13·6 tons per square inch (just above the fatigue range) produces practically no change.

1,118,200 reversals of this stress produces the appearance shown in fig. 12, which is still very little different from fig. 10 ; some slight extension of the dark area is, however, discernable, particularly near the crystal boundary. When the range of stress is below the fatigue range that portion of the crystal near the boundary frequently, but not always, appears stronger than parts further away from the boundary, and looks white under the microscope. In the present instance, these white borders have partly disappeared under the influence of the higher stress. The actual extension of the area over which visible slip has occurred is, however, very slight.

The dark areas in which slip-bands were visible formed a very small proportion of the total polished surface of the specimens, and large areas existed from which all signs of slip-bands were absent. This feature is shown in fig. 14 (Plate 31), which is a photograph of a small crack in the neighbourhood of the fracture of a specimen broken by 1,118,200 reversals of a range of stress of $\pm$ 13·6 tons per square inch.

The general features associated with fatigue cracks produced as described are illustrated in fig. 14. The course of the fracture passes through strained dark areas and light areas apparently unstrained, but there appears to be a tendency for the dark areas to be included for preference in the course of the fracture. The crack illustrated in fig. 14 occurred at a point in the specimen distant about 0·05 inch from and parallel to the fracture.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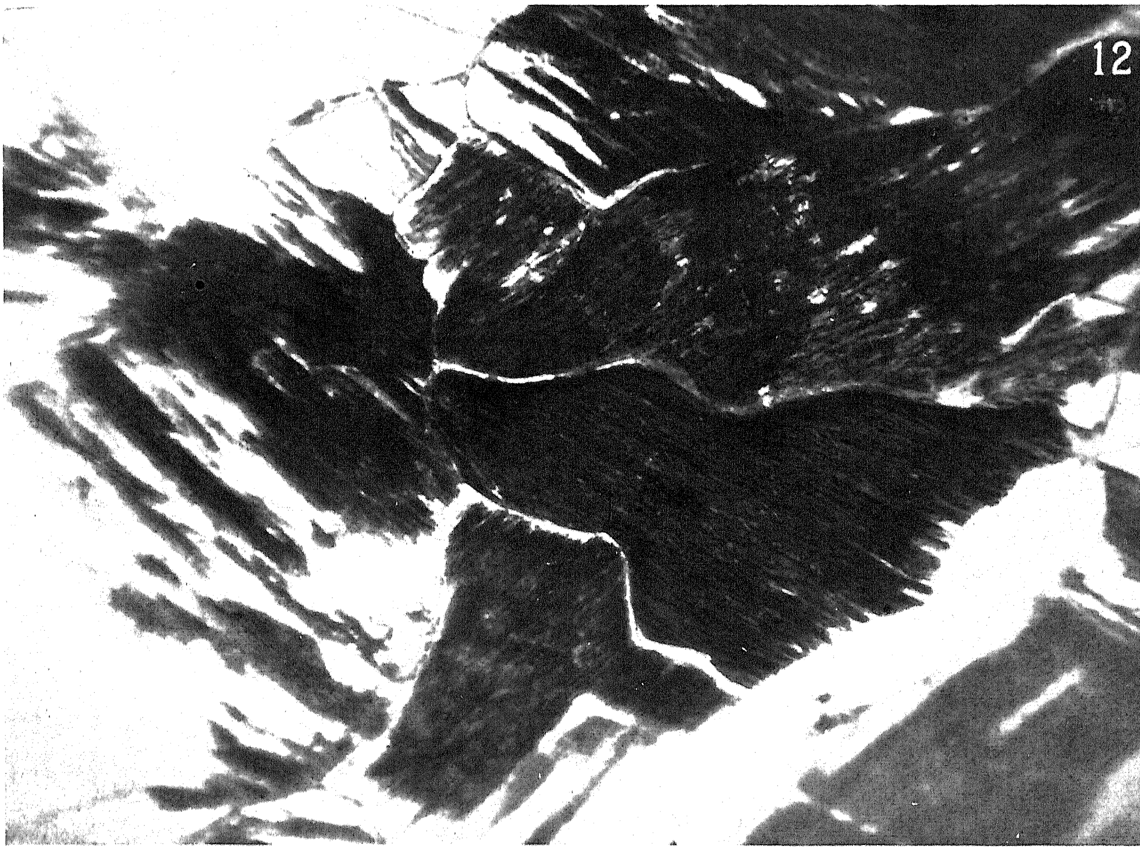
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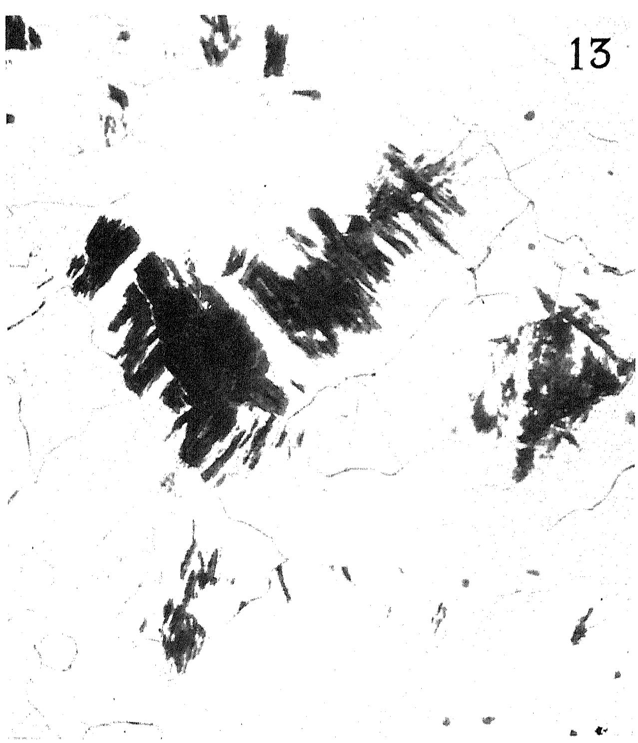
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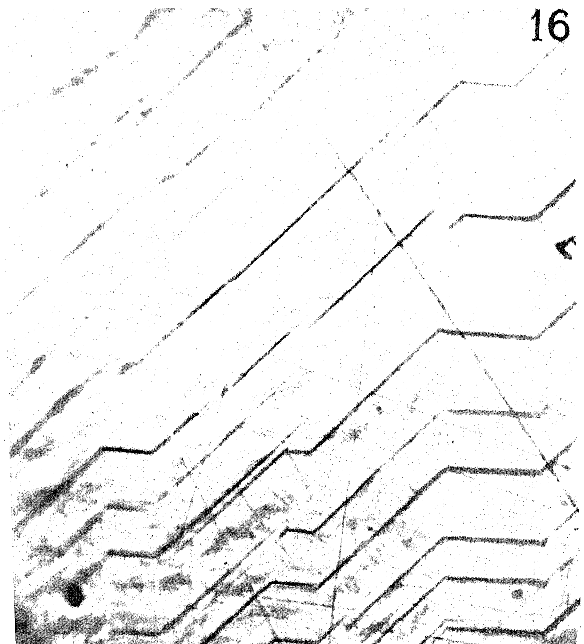
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The fatigue cracks are characterised by sudden changes in direction, as is seen in fig. 14. It will be noticed that the crack is spreading through a portion of the specimen from which massed slip-bands are absent. Examination under high magnification reveals signs of distortion round the crack, probably produced as the crack spreads owing to stress concentration at its ends.

Discussion of the Results.

The authors' results differ in some material respects from those of previous workers, in a manner that suggests that a different theory must be sought to explain the phenomena.

The dark bands in the authors' photographs suggest strongly that they have been formed in a different manner from that suggested by Ewing and Humfrey; they are found to consist of a mass of fine lines, close together, and appear to be masses of slip bands rather than one slip band that has been widened by attrition. Their multiple character can only be seen under very high magnification, and the photographs in the present paper have been taken at a magnification of 1,400 diameter; even when magnified to this extent many of the dark areas on the specimens could not be resolved. The authors' photographs, taken at low powers of the microscope, are very similar to those of Ewing and Humfrey, and it is thought the dark bands in the specimens of these workers would also have been found to be masses of slip-bands if they had been examined under still greater magnifications. The experiments of Ewing and Humfrey are, however, not conclusive evidence in favour of the view that repeated slipping occurs on the slip planes first formed, since slip-bands were found in some of their test-pieces under a range of stress that did not lead to failure, although, in their opinion, failure would probably have occurred had the number of reversals been sufficiently large. The authors' experiments show that in Armco Iron slip takes place under a range of stress less than the fatigue range; fig. 10 shows masses of slip bands in a sample subjected to a range of stress $\pm 0 \cdot 1$ tons less than the limiting range, the number of reversals being over 40 millions. There can thus be no doubt that in this material failure would not occur, and the authors' observations do not seem to be consistent with the theory that continuous slipping takes place on the planes first formed.

A comparison of figs. 10 to 12 shows that the appearance of the specimen subjected to a range exceeding the fatigue range is not essentially different from one subjected to stresses just within this range, and there seems to be

little doubt that the material is subjected, within the fatigue range, to deformation of the same character as that experienced when this range is exceeded.

In the opinion of the authors the observations described above do not indicate the presence of a mobile film on the planes at which slip occurs, and, indeed, there are some features connected with the deformation of metals under repeated stresses which are difficult to explain if a mobile film be postulated. It is, for example, not easy to understand why failure should not occur under repetitions of the stress necessary to produce the first slip within the material, and the authors' work has shown definitely that this does not occur. The mobile film was in the first place postulated in order to explain certain features connected with the behaviour of metal that had been overstrained, and particularly to explain the gradual recovery of elasticity after such overstrain. The same conception does not so readily explain the fact that recovery of elasticity can be attained in a relatively short time by subjecting overstrained material to reversals of stress at high speed ; if it be assumed that, during overstrain, slip has started, and that failure is due to the gradual widening by repeated slipping of mobile layers thus formed, setting of these layers would appear to be impossible while the cycles of stress are being applied, and the theory that the recovery of elasticity is due to this setting is inconsistent with the theory of failure.

The Behaviour of Metals under Repeated Stresses.

In order to account for the behaviour of metals subjected to repeated stresses, it is not necessary to assume that the nature of the deformation differs very greatly from that originally postulated by Beilby, who stated that, on the surface of the slip, a layer was formed, which, being stronger than the original crystalline material, prevented further deformation on that plane. He regards the formation of this layer as analogous to the process of melting, but any mobility of the material on the slip planes is of a very transitory character, and disappears immediately slip is completed. The stiffening of the material through the formation of "amorphous metal" on the slip planes is considered gradually to increase the strength by removing those planes that are particularly unfavourably situated for withstanding the applied stress ; one by one these are strengthened, and the resistance of the material to the particular stress is increased. Finally, it may be presumed that a point is reached at which a crack is formed through the accumulation of this hard non-plastic material, and the metal fails. It seems probable, in the light of recent work, that the mechanism of deformation in metals is insufficiently understood

to enable any comprehensive theory of *failure* to be at present postulated. In the authors' opinion, failure under repeated stresses does not differ essentially from failure under static stresses; when a sufficient stress is applied, slip occurs within favoured crystals within the material, resulting in a certain amount of local strain-hardening, and, when the stress is reversed, further slip takes place, but *not* on the original slip-band, which has been strengthened by the previous slip. This process is repeated, and, if the range of stress is not too great, the metal may become sufficiently strengthened to withstand an indefinite number of reversals of that range of stress without further slip occurring. In this way the formation of masses consisting of a very large number of slip-bands would be readily understood, and the formation of slip-bands within the fatigue range explained, for it is no more difficult to picture a material being strain-hardened under repeated or alternating stresses than it is to picture the same condition under static stresses. The metal can, in fact, be cold-worked under alternating stresses, without fracturing, in exactly the same manner as it can be cold-worked by tensile stresses.

If this view is correct, it would be anticipated that in all ductile materials considerable deformation under reversed stresses would occur within the fatigue range, and that failure would only take place if the material had been overstrained to a considerable extent, a result that has been confirmed experimentally for iron, nickel, copper and aluminium. It is, however, evident that the amount of such over-straining that a metal can withstand is limited and that ultimately a point must be reached at which a crack is formed. In the authors' experiments on iron, straining has been extremely local, because only those portions that were particularly favourably disposed to slip have been appreciably affected; it is, probably, this *local* overstraining that ultimately causes a crack to start.

The exact manner in which a crack begins is not here considered. Beilby* has suggested a mechanism by means of which such a crack might be formed as a result of the change from the crystalline to the amorphous state, and a somewhat similar view has more recently been expressed by Griffith†; but the authors' view does not depend on the correctness of the explanations of Beilby* and Griffith,† or of the general theory of strain-hardening by the formation of amorphous metal, although it is consistent with them; it makes no assumption other than that strain produces, on the surfaces of slip, a

* Beilby, *loc. cit.*

† Griffith, 'Phil. Trans.,' A, vol. 221, pp. 163–198.

resistance to further strain, and that the amount of straining that a metal will withstand is limited.

According to this view, failure under repeated stresses and failure in static tension are preceded by exactly the same process. In both cases failure is preceded by the plastic straining of the metal, accompanied by slip, and a crack forms when this straining reaches a limiting value. In the tensile test, the actual maximum applied stress is high because slip is only possible in one direction along any particular set of planes of a crystal, but under alternating stresses slip is possible in both directions along any particular set of planes, although it is assumed to occur only in one direction on any one plane. The fact that the fatigue range has been found by many workers to be approximately proportional to the ultimate tensile strength is readily understood if the mechanism of failure in the two cases is identical.

The authors' experimental observations are not greatly different from those of Ewing and Humfrey, or of Stanton and Bairstow, and the same explanation would fit the observations of those workers. Stanton and Bairstow only examined the structure after subjecting the material to stresses exceeding the fatigue range, but Ewing and Humfrey observed slip-bands formed by a range of stress less than the fatigue range, although at the time they did not realise the significance of this observation.

Overstrain.—Creep and Elastic After-working.

There are certain aspects of overstrain that now require reconsideration, and, in the first place, it will be convenient to consider overstrain by simple tension.

The phenomena connected with overstrain fall naturally under two heads:

(*a*) The behaviour during the application of the stress.

(*b*) The behaviour during the removal of the stress.

When a load exceeding the primitive tensile yield-stress is applied to a metal, the well-known type of load-elongation diagram is obtained. Plastic deformation ensues, but the amount of the total deformation depends on the time of application of the stress; there is a definite "creep," and the elongation increases at a decreasing rate. In iron and steel this creep is relatively small, but in some metals it is very considerable. In the authors' view this creep is ordinary plastic strain by slip, spreading from crystal to crystal.

When a piece of metal consisting of a mass of crystals is subjected to an applied stress, the crystals are at first extended elastically, *i.e.*, without any

permanent distortion of the space-lattice, the amount of the stress, and consequent strain, in the case of any particular crystal will depend on the inclination of the axes of the crystal to the direction of the applied stress, and the manner in which the deformation of surrounding crystals re-acts upon the particular crystal; in any crystal the unsymmetrical shape of itself, and its bounding surfaces with its neighbours, are so complicated that it will seldom happen that the stress on any one series of gliding planes within the crystal is uniform throughout the crystal. The stress on any one gliding plane, in fact, need not be uniform. The internal stresses within the mass of the metal will be extremely complex.

When the applied stress reaches a certain value, which may in some cases be very low, plastic yielding will occur along a plane that is favourably situated, *i.e.*, that is highly stressed under the conditions of the loading. This will cause a local redistribution in the internal stresses within the metal, since the shape of that particular crystal will have been altered, and in consequence, its exact relations to its neighbours will have changed. If one plane should be exceptionally highly stressed, it is conceivable that it alone will be affected, and that no further yielding will occur, unless a greater strain is applied; for small plastic strains it appears that exceptionally "favoured" planes may be rare, and slip under any one load will be but slight; it may not be measurable. In such a case departure from true elasticity (if such exist) would be very gradual, and there would be little or no "creep" under any load slightly exceeding the "elastic limit."

The re-distribution of stress in the crystal, which results from slip, may cause an increase or decrease of stress in its immediate neighbourhood; in general, it will do both at different portions of the crystal, and a local increase in stress of this kind, acting on a suitably placed cleavage plane, may, and frequently will, cause further slip to occur, involving a further re-distribution; this process will, in fact, go on until no more favourably placed cleavage planes remain. In such a case the strain will "creep" under the applied stress. This creep may become cumulative under any one load, and re-distribution as each plane slips may so alter the stresses that another slips, and so on, until all the crystals have been affected; such a case would appear to occur in iron and soft steel, in which sudden extension of this kind occurs at the "yield point." The extension at the yield-point is so great that most of the crystals must be plastically deformed; yield only seems to be stopped when these crystals have been plastically strained (strain-hardened). In other cases sudden yielding will not occur, but the "creep" will gradually reach a

maximum. It is probable that a long time usually elapses before creep ceases entirely.

The amount of this creep will, in general, increase as the stress is increased, and finally a load is reached at which it does not stop, and the metal breaks. (Certain abnormal cases of fracture, such as by season cracking, are not included.)

It will be seen that this explanation is sufficient to cover the initial "peak" load at the yield-point coupled with the fact that further creep takes place even if the load is reduced. The peak load causes the primary large plastic deformation involving large internal strains, and the subsequent creep is the result of internal strain adjustments due to these large internal strains distributing themselves throughout the mass of unequally strained material.

In the authors' view, the material is immediately strain-hardened by the production of permanent deformation, and it is unnecessary to postulate that the slip-planes are the seat of a temporarily mobile film (at least, the temporary mobility need not last appreciably longer than is required to form any such film). The loss of elasticity of such material on re-loading can only be explained in connection with the behaviour during *unloading*, for it is found that, if the load be removed before the creep is allowed to complete itself and immediately re-applied, the total strain produced by this re-application exceeds the strain under the first application. Now, unless some change occurs during unloading, there seems no reason to suppose that, on re-loading, the internal condition of the material is different to that after the first application of the load, even if mobile layers on the slip planes be postulated, and the same stress ought to produce the same strain. It would thus appear that overstrain in tension is not directly responsible for the loss of elasticity, and such overstrain can only increase the elastic range in tension; *if the metal could be unloaded without altering it in any way, it appears probable that the material would be elastic* (*as consistent with elastic hysteresis*) *up to the same range of strain* (*not stress*).

Behaviour during Removal of the Applied Stress.

As a result of the loading, plastic deformation has been caused, resulting in internal stresses and strains which by a process of adjustment have resulted in "creep." Let us imagine the adjustment process has been carried to the stage when the creep has stopped. This must mean that at any point within the material the residual strain is insufficient to cause further slip. But this internal strain will be by no means uniform throughout the mass, and in some

places it will be just insufficient to cause slip. It would be expected that the slipped portions are freer from strain than those neighbouring portions which have as yet suffered no plastic deformation. But these portions are strongly bonded together, and when the process of unloading occurs, it will be exactly similar to that of loading. When the load has been reduced by a greater or lesser amount, plastic deformation will take place in portions originally free from slip. When zero load is reached and maintained, the internal strains due to this latter slip will now re-distribute themselves by further slip, but the resulting creep will now be negative (elastic after-working). Thus creep at full load and elastic after-working at zero load are considered to be essentially the same phenomenon, and it is, therefore, unnecessary to designate the one "overstraining" and the other "recovery." *From the point of view of attaining "elasticity" with this cycle of loading,* i.e., *the attainment of a cyclic state involving "hysteresis," but not increase of "total permanent set," both "creep" and "elastic after-working" are definitely processes of recovery and are identical.*

Confirmation of this view that elastic after-working and recovery of elasticity involve straining of the material is obtained by a consideration of the mechanical properties of the "recovered" material. If stress is the essential factor, and recovery is simply the setting of mobile layers produced by that stress, then "recovered" material should be elastic up to the *original maximum applied stress*; on the other hand, if the material has been hardened by strain, then it should be elastic, after recovery, up to a stress corresponding to that amount of *strain.*

Unfortunately, in published results only applied stresses have been measured, but the facts are nevertheless decidedly in accordance with the second supposition, although quantitative data are not available: they may be summarised as follows:—"If the overstraining load is applied momentarily the new elastic limit is less than the overstraining load; but if the load is prolonged the elastic limit after recovery *exceeds any load* previously applied to the specimen"*; recovery is thus only indirectly related to the applied stress, but it is intimately connected with the resulting strain, and recovery therefore involves strain-hardening.

An interesting experiment reported by Muir† may be regarded as indicating that the results of the processes of loading and unloading a specimen are essentially the same. He took two specimens of the same steel and overstrained them to the same extent; one specimen was allowed to rest under

* R. H. Greaves, 'Report R.D. 34' (Research Dept., Woolwich, 1922).

† J. Muir, 'Phil. Trans.,' A, vol. 193 (1900).

the maximum load for 40 days, while the other was allowed a similar rest free from any externally applied stress. After this period the one specimen was carefully unloaded and the other loaded, stress-strain curves being taken. The curves are reproduced in fig. 17; it is seen that the behaviour of the

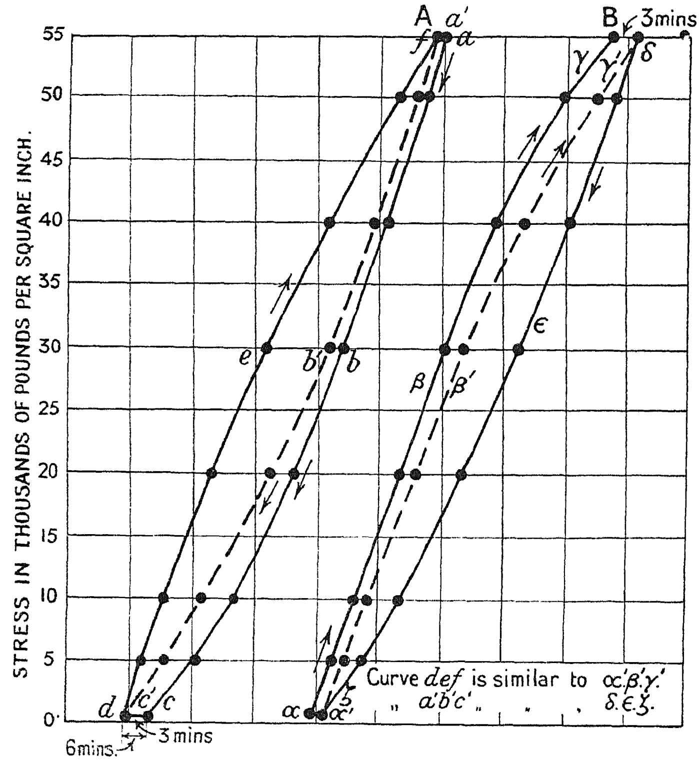

FIG. 17.—A. Overstrained specimen, after resting 40 days at stress of 55,000 lbs./in.².
B. Overstrained specimen, after 40 days free from stress.

specimen that has been stored under the load was exactly similar to that stored free from externally applied stress; in both cases the stress-strain curve is nearly elastic for a considerable distance, after which it departs from the straight. On reversing the cycle it is found that the stress-strain relation is nowhere linear; *in the one case elasticity has been lost through straining on re-loading*; *in the other case it has been lost by straining on un-loading.* The processes are identical in character, the signs of the stresses only being different. It is evident that the effect of unloading is just as injurious to the metal as the loading part of the cycle.

The "Cyclic State."

(*a*) *Within the Fatigue Range.*

If, when a specimen is subjected to ranges of stress less than the limiting range, observations are made of the relation between stress and strain (by plotting the usual hysteresis loops), it is frequently found that a considerable number of reversals of the stress must be applied before the hysteresis loop becomes closed, and the material attains a "cyclic state"; at the same time the material becomes elastic (as consistent with elastic hysteresis) over this range of stress. According to the authors' view the attainment of the cyclic state is accompanied by plastic deformation and strain-hardening. The material attains a cyclic state because *plastic strain ceases,* the metal having been strain-hardened, so that it can permanently resist the applied stress without further plastic strain; such material is, of course, elastic up to that degree of strain. The process is similar to "creep."

(*b*) *Above the Fatigue Range.*

The behaviour when the range of stress exceeds the limiting range differs from that when this range is not exceeded only in that plastic strain never stops; when the range only slightly exceeds the fatigue range, plastic strain may decrease until it becomes very small at each reversal, but it can never cease entirely, and, finally, a crack forms at one of the locally strained regions of the material.

The above explanation is in keeping with the work of Mason,* who has shown that, if the range exceeds the fatigue range, the range of strain increases at a decreasing rate, but *never* attains a constant value. When the fatigue range is exceeded, the material never actually passes into the cyclic state, since plastic strain never entirely ceases, although for practical purposes it is convenient to apply the term "cyclic state" when the hysteresis loop has attained a nearly constant value.

Failure under Ranges of Stress whose Mean Value is other than Zero.

Fig. 18 is a reproduction of the well-known diagram of Bairstow.† With any superior limit of applied stress, there is a corresponding inferior limit of stress below which the material must not be unloaded if ultimate fracture is

* Mason, 'Proc. Inst. Mech. Engrs.,' 1917.

† L. Bairstow, 'Phil. Trans.,' A, vol. 210 (1910).

to be avoided under repeated loading and unloading. This fact, which has been confirmed by other workers, is extremely difficult to explain from a

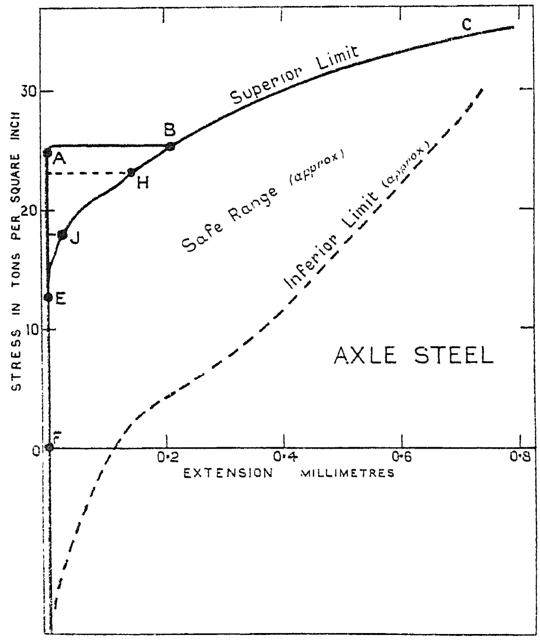

FIG. 18.—F, A, B, C. Load elongation from static tensile test.
F, E, H, C. Total elongation, material in cyclic state. (After Bairstow.)

consideration of stress alone. The views here presented offer a more satisfactory explanation. The repeated application of the superior limit of stress produces plastic deformation in the material, and Bairstow has shown that, when the cyclic state is attained, the total extension at the superior stress under alternating stresses is approximately equal to the extension obtained under the same stress in a direct tension test. Plastic deformation, with resulting internal strain, is thus the result of the application of the superior stress. If now the process of unloading can be shown to be precisely similar to that of loading, and the criterion of failure be that the material shall not be subjected to more than a limiting strain, it is at once obvious that, provided the inferior stress of the cycle is not *less* than a certain limiting value, failure will not result; a truly cyclical state will be attained and plastic deformation will cease. For any material, therefore, the superior limit and the corresponding safe range of stress would be expected to be connected in a regular manner. Owing to the essentially different stress-strain curves obtaining with different materials it would not be expected that any definite

relation, such as that of Gerber or Goodman, would prove to be generally true for all materials, and existing experimental evidence confirms this view.

Hysteresis.

The authors' views are not inconsistent with the facts relating to hysteresis, which is now known to occur with cycles of stress well within the limiting range; it is, in fact, suspected that it occurs, in most materials, under all ranges of stress.* The authors found it in iron with all ranges exceeding $\pm$ 4·26 tons per square inch. Elastic hysteresis of this kind must be explained without reference to plastic strain or amorphous mobile films, and elastic hysteresis does not appear to be connected with failure under repeated stresses. Bairstow's work must be modified so as to be consistent with the existence of elastic hysteresis.

Hysteresis under a range of stress exceeding the fatigue range, or within the fatigue range before a cyclical state is established, must be regarded as partly elastic and partly plastic; the plastic hysteresis being due to the occurrence of slip on the gliding plane of the crystal at each reversal of the applied stress.

Heat Bursts.

The occurrence of "heat bursts" accompanying a sudden increase in stress, which was discovered by Hankins, in nickel, and confirmed by Haigh, who then extended the work to other metals, is not inconsistent with the reasoning offered above. The *steady evolution of heat which is observed at all ranges of stress* is quite a different phenomenon from that of the heat bursts, being merely an indication of the elastic hysteresis. The transient heating within the fatigue range is due to the process of plastic strain by slip, and, when this process is completed, the material can withstand similar cycles of the same stress without further plastic strain, and the heat evolved falls to the steady value corresponding to the elastic deformation for the particular stress. If, however, the range exceeds the fatigue range of the material, some portion of the heat generated will always be due to plastic strain.

Under the application of cycles of specific strain, instead of specific stress, different results would be expected. If the strain at each reversal is controlled by the conditions of the test, sudden bursts of heat would become impossible. Very slight "peak" values *might* be obtained, even using cycles of specific strain, but they would be expected to be insignificant compared to those obtained by applying specific stress.

* Guest and Lea, 'Roy. Soc. Proc.,' A, vol. 93 (1916–17).

THE BEHAVIOUR OF MATERIALS OTHER THAN IRON.

Although the experimental results so far described have been obtained with Armco Iron, the authors have obtained similar results with other materials, and it cannot be supposed that Armco Iron is in any way exceptional in this respect. These additional results are not now described fully, but a few photomicrographs are given.

In the case of mild steel, whose properties under repeated stresses were accurately known, masses of slip-bands were found when the range of stress (mean stress = zero) was *less than the range of the static limits of proportionality*, as determined with great accuracy by the ordinary Martens extensometer. Fig. 15 shows the material after being subjected to 10×10^6 reversals of a range of $\pm$ 14·9 tons per square inch, the static limit of proportionality being 15·2 tons per square inch; another specimen of the same material withstood 250×10^6 reversals of $\pm$ 15·9 tons per square inch, without breaking, and the fatigue range must therefore exceed this value. (See Pl. 31.)

Experiments on copper, possessing a fatigue range of $\pm$ 5·5 tons per square inch, showed that many slip-bands were produced by applying a range of stress of $\pm$ 1·1 tons per square inch; fig. 16 shows slip-bands formed by a range of $\pm$ 2·2 tons per square inch.

In aluminium and nickel, the formation of slip bands has not been directly investigated, but the fatigue range has been found to exceed the range of the static limits of proportionality. In the case of aluminium the authors have had the privilege of determining for Professor H. C. H. Carpenter, F.R.S., the fatigue range of some test pieces cut from a single crystal, in which it was also found that the fatigue range exceeded the range of the static limits of proportionality. This case is particularly interesting since it confirms that the phenomena described are associated with the crystals themselves, and do not depend primarily on the presence of bounding surfaces between different crystals.

In the case of certain hardened steels it is also found that the fatigue range far exceeds the range of the static limits of proportionality.

The experimental results herein recorded are not peculiar to Armco Iron, and the authors trust that the views elaborated above will be deemed worthy of consideration as being of general application.

ACKNOWLEDGMENTS.

The authors wish to thank Sir Joseph Petavel, K.B.E., F.R.S., Director of the National Physical Laboratory, and Dr. T. E. Stanton, F.R.S., and Dr. W.

Rosenhain, F.R.S., Superintendents of the Engineering and Metallurgical Departments, in which the work has been carried out, for their interest in this research.

To Prof. H. C. H. Carpenter, F.R.S., they are indebted for permission to refer to the work done for him on single crystal test-pieces of aluminium ; and they wish finally to acknowledge the help of Mr. W. M. Wheeler, laboratory attendant in the Metallurgical Department, whose skill in preparing the sections required for the metallographic work has greatly hastened the course of the research.

On the Velocity of the Positive Ions in the Crookes Dark Space.

By F. W. Aston, F.R.S., Fellow of Trinity College, Cambridge.

(Received November 9, 1923.)

Notwithstanding the great volume of published investigations on the electric discharge in gases, the nature of the negative glow and the mechanism by which the current is carried across the Crookes dark space at moderately low pressures are still matters of speculation. Some years ago, in describing investigations on the latter phenomenon, I drew attention to the outstanding difficulties in the way of formulating a workable theory.* One of these difficulties was an apparently hopeless discrepancy between two values for the velocities of the positive ions at the surface of the cathode, the one calculated from their measured space charge and the total current passing through the tube, the other obtained by extra-polation from the mobility measured at higher pressures. On reconsideration of the problem, I now recognise that the latter value was definitely wrong, and in this paper will show that if instead the velocity is calculated from more reasonable assumptions the discrepancy is almost entirely removed.

The mean drift velocity of positive ions in a gas under an electric force varies directly with the electric force and inversely with the pressure of the gas. A linear relation has been shown experimentally to hold from atmospheric pressure down to pressures of the order of 1 mm. of mercury, so long as the electric fields are so small that the mean drift of the ions is insignificant

* F. W. Aston, 'Roy. Soc. Proc.,' A, vol. 87, p. 448 (1912).

compared with their velocity of thermal agitation. In the particular circumstances now under consideration we are concerned with the movements of positive ions near the surface of the cathode in the Crookes dark space, where the electric field may be as high as 1000 volts per cm. in gas at pressures of the order of 0·1 mm. of mercury. Under these conditions the velocity of thermal agitation becomes negligible compared with that acquired by the ion between successive collisions, so that a linear extrapolation is quite unjustifiable.

The best means of obtaining an approximate value of the mean drift under such conditions is clearly to neglect the velocity of thermal agitation altogether, and to suppose that the ion is stopped completely by each collision with a gas molecule and falls freely towards the cathode between its successive collisions.

If m is the mass and e the charge of the ion moving in a field X, the mean rate of progress k_λ towards the cathode will be given by

$$k_\lambda = \tfrac{1}{2}\sqrt{\frac{2eX\lambda}{m}} \tag{1}$$

where λ is the mean distance moved towards the cathode between two successive collisions. This distance will be somewhat greater than the ordinary "mean free path" of the molecule, on account of the high speed, but will be reduced by the fact that the particle is charged. We shall not therefore be far wrong if we take for λ the ordinary molecular mean free path at the pressure concerned.

We may also estimate the mean velocity of the positive ions towards the cathode in a totally different way from considerations of the total charge they bring up to it. If ρ is the density of positive electrification on the ions just in front of the cathode, and i the current carried by them to each sq. cm. of its surface, then their mean velocity k_ρ will be given by

$$k_\rho = \frac{i}{\rho}. \tag{2}$$

If we give i the value of the total current passing in the discharge we shall obtain a maximum value for k_ρ. So far it has not been found possible to measure directly the percentage of current carried across the dark space by electrons originating at the cathode surface. Most of the indirect experimental evidence favours a very small value. My own experiments with a pierced cathode* suggested about 50 per cent., but little reliance can be placed on them, for the effects measured were clearly complicated by an intense local

* F. W. Aston, 'Roy. Soc. Proc.,' A, vol. 96, p. 200.

ionisation in the region of the slit. For the present argument we shall compare the values of k_λ obtained from (1) with the maximum values of k_ρ given by supposing the whole current carried by the positive ions.

The distribution of electric force in the dark space has been measured directly by shooting a beam of high-speed cathode rays across the discharge.* The range of pressures, for any one gas, which could be employed were, unfortunately, small and of the order corresponding to dark spaces of about 3 cms. Aluminium electrodes were used and measurements were made in several different gases over a considerable range of current density. The field in all cases was found to vary linearly with the distance from the edge of the negative glow, in which it was zero, to the surface of the cathode where it was a maximum. Under the particular conditions, namely, high current density and absence of positive column, the total fall of potential across the dark space was shown equal to the voltage between the electrodes.

If we assume this linear distribution of the electric force, we can calculate the values of X and ρ in the dark space from measurements of its length D and the voltage drop V across it. For in these experiments the diameter of the cathode is great compared with D, so that the surface of the cathode and the negative glow can be treated as infinite plane conductors. The field in the negative glow is zero, hence the total positive charge in the dark space must exactly equal the negative charge on the face of the cathode. From this it follows that, if ρ is the density of positive electrification and X the electric force at any point x from the negative glow,

$$X = 4\pi \int_0^x \rho dx.$$

But experiment shows that X varies as x, hence ρ is constant and the field at the surface of the cathode is $4\pi\rho D$. But this field also is 2VD from the linear law, so that $\rho = V/2\pi D^2$.

There is no lack of data for the purpose of calculating the numerical values of k_ρ and, if we assume a value of m, those of k_λ also, for the relations between i, V and D have been determined in many gases over considerable ranges of pressure. The first set of results we shall consider are those obtained by the use of an aluminium guard-ring cathode and tabulated for a dark space of 1 cm. under a standard current intensity of 0·1 milliampere per sq. cm.†

* F. W. Aston, 'Roy. Soc. Proc.,' A, vol. 84, p. 526.

† F. W. Aston and H. E. Watson, 'Roy. Soc. Proc.,' A, vol. 86, p. 168.

Table I.

Gas.	m.	p in 10^{-2} mm. Hg.	L in 10^{-6} cm.	λ in mm.	V in volts.	$2\,\mathrm{V}\lambda/\mathrm{D}$.	K_λ in 10^6 cms./sec.	ρ in E.S.U.	K_ρ in 10^6 cms./sec.	$\mathrm{K}_\lambda/k_\rho$.
H_2	2	46·8	18·3	0·298	266	15·8	1·93	0·141	2·13	0·91
He	4	70·6	28·5	0·307	395	24·2	1·70	0·209	1·43	1·19
He	4	52·5	28·5	0·413	412	34·0	2·01	0·218	1·38	1·45
CO	28	17·5	9·27	0·404	489	39·5	0·82	0·259	1·16	0·71
N_2	28	11·3	9·44	0·635	434	55·2	0·97	0·230	1·30	0·75
O_2	32	11·4	9·95	0·663	444	58·9	0·94	0·235	1·27	0·74
Ne	20·2	18·6	19·3	0·790	545	86·0	1·43	0·289	1·37	1·37
Ar	39·9	8·2	10·0	0·926	594	119	1·19	0·315	0·95	1·25
Ar	39·9	8·3	10·0	0·915	610	112	1·16	0·323	0·93	1·25
Kr	82·9	8·3	9·49	0·867	745	129	0·86	0·395	0·76	1·13
Xe	130	5·9	5·61	0·723	1025	148	0·74	0·544	0·55	1·34

In the above table m is the mass of the positive ion assumed and is expressed in terms of the oxygen scale. p, the pressure, is in hundredths of a millimetre of mercury. L is the ordinary molecular mean free path at atmospheric pressure in 10^{-6} cms. λ is the mean free path at pressure p in mms. V is the potential across the dark space in volts. In the next column is the voltage per mean free path $2\,\mathrm{V}\lambda/\mathrm{D}$ calculated from the electric field at the surface of the cathode. This represents the mean voltage drop between successive collisions. k_λ is calculated from equation (1) and is expressed in 10^6 cms. per second. The values of ρ are calculated from the expression $\mathrm{V}/2\pi\mathrm{D}^2$ and given in absolute electrostatic units. k_ρ is derived from equation (2) by putting in the value of the total current 3×10^5 E.S.U. per sq. cm. of cathode; it is expressed in the same units as k_λ. In the last column are given the ratios between the two values of the velocity. If all the assumptions were rigidly true, these ratios would represent the fraction of the current carried by the positive ions.

Two sets of figures are given for helium and argon. In each case the second set refers to the purer specimen of gas. Pure helium is, however, very unsuitable for dark-space measurements (*loc. cit.*), so that the figures obtained from it do not possess very much significance.

It will be seen that, far from showing marked discrepancies, the two sets of values for the velocities, calculated so differently, are not only of the same order but in some numerical agreement, notwithstanding the fact that the

masses vary over a range of more than 60 to 1. In all the monatomic gases k_λ is greater than k_ρ, while in the diatomic ones the reverse is the case. This difference would be removed to some extent by the assumption of a smaller value of m, since it is quite certain that a considerable percentage of the current in diatomic gases is carried by atoms.

It is not proposed to found a new theory of the dark space on so simple an expression for the velocity of the positive ions, which at the best is only a rough approximation. There is therefore no necessity to tabulate all the other numerous cases which have been worked out. In general, the ratio k_λ/k_ρ decreases with decrease of pressure at constant current and also decreases with increase of current at constant pressure in the same gas.

One particular set of figures seems worth recording, as it shows a remarkably close agreement between the two values over a large range. These are given in Table II, and refer to results obtained at Birmingham in 1907 with an aluminium guard-ring cathode in helium containing traces of impurities sufficient to cause it to give consistent dark-space measurements.

Table II.

p in 10^{-2} mm. Hg.	i in arbitrary units.	D in cms.	V in volts.	$2\,V\lambda/D$.	K_λ in 10^6 cms./sec.	ρ in E.S.U.	K_ρ in 10^6 cms./sec.	K_λ/k_ρ.
80·0	60	0·793	392	26·7	1·77	0·333	1·57	1·13
51·0	60	0·972	489	42·6	2·25	0·259	2·19	1·03
51·0	30	1·122	365	27·6	1·81	0·150	1·66	1·09
37·5	40	1·450	580	46·3	2·34	0·146	2·40	0·97
33·0	60	1·420	690	63·6	2·74	0·182	2·88	0·95
33·0	30	1·600	571	46·9	2·36	0·118	2·23	1·06
22·9	40	1·990	882	94·5	3·35	0·118	2·97	1·13

In this table i is expressed in arbitrary units and D is given in cms., the units for the other values are the same as in Table I.

It is of interest in this connection to compare the various equations connecting the values of i, p, D and V, which we obtain by assuming different

relations between the velocity of the positive ions and the electric force acting upon them. In order to get these equations we have to neglect not only the density of the electrons in the dark space, which is reasonably justifiable, but also the current carried by them at all points in it, a very doubtful assumption. If, as in my original theory of the dark space,* the mean velocity is taken as simply proportional to the force X, we get, for a given gas

$$ipD^3V^{-2} = \text{const.} \qquad (3)$$

If the mean velocity is that indicated in the present paper, which is proportional to the square root of the force,

$$ipD^{5/2}V^{-3/2} = \text{const.} \qquad (4)$$

If, as has recently been suggested,† the ions behave as though falling freely in a vacuum from negative glow to cathode,

$$iD^2V^{-3/2} = \text{const.} \qquad (5)$$

Equation (3) agrees best with the actual dark-space measurements over a certain range but it cannot be physically true. Equation (4) is not in such good agreement with these measurements. Equation (5) gives too high a value of ionic velocity at the surface of the cathode, 10 to 15 times too high in the cases of hydrogen and helium, for it to be considered as an explanation of the particular facts now under discussion.

None of these assumptions give, even approximately, the linear distribution of the electric force found by direct experiment. Indeed, it is clear that no assumption involving velocity as a direct function of the field can possibly do this, so that we are driven to the conclusion that though the current carried by electrons may be very small near the cathode it cannot be negligible at all points in the dark space. The problem is complicated in the cases of the diatomic gases by the occurrence of atoms as well as molecular ions, and in all cases except those of hydrogen and helium by the occurrence of ions carrying more than one charge. The reason why helium gives the consistent results given above may possibly be connected with its peculiarity in both these respects.

It is now generally accepted that positively charged particles passing through a gas do not necessarily retain their identity, but by capturing and losing

* F. W. Aston, 'Roy. Soc. Proc.,' A, vol. 79, p. 80 (1907).

† J. W. Ryde, 'Phil. Mag.,' vol. 45 p. 1150.

electrons may lose and regain their charge from time to time. How this effect is to be allowed for is not clear. The data available on dark-space measurements with cathodes of metals other than aluminium cannot consistently be applied to the problem with which this paper is concerned, for the latter is the only metal for which the distribution of the electric force in the dark space has been experimentally determined.

It appears exceedingly probable that a certain percentage of positive ions formed in the negative glow actually do reach the cathode with the full velocity corresponding to a free fall. At lower pressures this has been experimentally demonstrated by positive-ray analysis. On the other hand the figures quoted in this paper indicate that a much larger proportion reach the cathode with velocities ranged about that derived from a free fall between successive collisions. A direct experimental determination of the distribution of velocities among the ions striking the cathode suggests itself, but the problem is by no means easy. One attempt at least has failed,* but the rapid improvement in vacuum technique should enable positive-ray analysis to be applied with good hope of success to this very interesting problem.

* F. W. Aston, 'Roy. Soc. Proc.,' A, vol. 96, p. 204.

On the Theory and Testing of Right-Angled Prisms.

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(Received January 26, 1923.)

It is well known that right-angled prisms may be inaccurate in two important respects, which may be illustrated in the accompanying figure (fig. 1). In the first place, the angle at A may not be strictly a right angle, and if its true value is $90°+\varepsilon$, we shall call ε the "angular error" of the prism.

The plane of the face BCFD may not be exactly at right angles to the end ABC. If the inclination of these planes is $90°+\eta$, we shall call η the

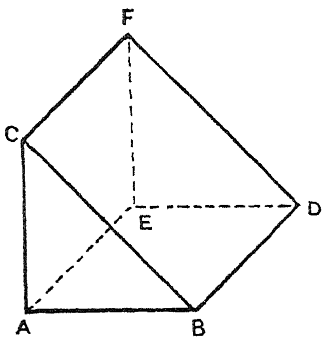


FIG. 1.

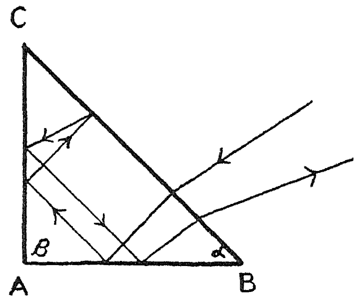


FIG. 2.

"pyramidal error" of the prism. Special methods of determination of this error have to be devised; and although a method was given by Coddington, it has not been incorporated subsequently into any optical text-book. Although in use at the present time, it has been applied quite erroneously in many cases, and we propose therefore to begin the present note with a full account of the method and the approximations involved in it. For Coddington himself did not give any proof of the formulæ involved.

Fig. 2 shows the case in which Coddington's formulæ may be used legitimately. A ray strikes the larger face normally and enters the prism. It is reflected from each of the other faces internally, then from the larger face, and finally again from each of the others. It emerges from the larger face parallel to its original direction if the prism has no error of either type.

Let n be the index of refraction of the material, and ε and η the two errors

already defined. Then the inclination of the final emergent ray to its incident direction is, when they are small,

$$4n\sqrt{\varepsilon^2 + \eta^2}.$$

This is the resultant of two independent (to the first order) deviations.

In the absence of pyramidal error, the emergent ray is in the plane ABC with the incident ray, with a deviation $4n\varepsilon$. When there is no angular error, the plane through the incident ray (in the plane ABC) and the emergent ray is perpendicular to ABC, and the deviation is $4n\eta$.

In the presence of both errors, these deviations are superposed, to the first order.

In the experimental arrangement, parallel light may be directed normally to the face BC from an object o at the focus of a system of length f, and the emergent rays collected in the focal plane to another point o'. If $o\mathrm{P}o'$ is the focal plane, and $o\mathrm{P}$ is parallel to the edge BC,

$$o\mathrm{P} = 4n\varepsilon f, \qquad \mathrm{P}o' = 4n\eta f,$$

and these formulæ are the basis of measurement of ε and η.

Theoretical Discussion.

It is desirable, in the proof of these formulæ, to take a quite general view in the first place. We shall accordingly suppose the prism to be of any form, with angles α and β at A and B in the face ABC, and with the larger face at an angle δ to the plane ABC.

We may take A as origin, AB as axis of x, the axis of y through A in the plane ABC, and z perpendicular to ABC, using the method of direction cosines.

The directions of the normals to the three faces are

(1) face AB, $(0, 1, 0)$

(2) face AC, $(\sin\beta, \cos\beta, 0)$

(3) face BC, $(\sin\delta \sin\alpha, \sin\delta\cos\alpha, \cos\delta)$.

These can be verified at once. We shall also require the following theorem, whose importance in investigations of this nature has already been indicated by R. A. Sampson.

If a ray in the direction (l, m, n) falls on a point of a surface at which the normal is in the direction (λ, μ, ν), the direction of the reflected ray is (l', m', n') where

$$l' = 2\lambda\cos\theta - l, \quad m' = 2\mu\cos\theta - m, \; n' = 2\nu\cos\theta - n,$$

θ being the angle of incidence, with $\cos\theta = l\lambda + m\mu + n\nu$.

This can be proved at once by the laws of reflection. For we have

$$\lambda l' + \mu m' + \nu n' = 2 \cos \theta \,(\lambda^2 + \mu^2 + \nu^2) - (l\lambda + m\mu + n\nu)$$
$$= 2 \cos \theta - \cos \theta = \cos \theta,$$

so that the angle of reflection is also θ. Moreover

$$\begin{vmatrix} l' & m' & n' \\ l & m & n \\ \lambda & \mu & \nu \end{vmatrix} = 2 \cos \theta \begin{vmatrix} \lambda & \mu & \nu \\ l & m & n \\ \lambda & \mu & \nu \end{vmatrix} = 0,$$

so that the three rays are in one plane.

We may now apply this theorem to any number of reflections in fig. 2.

(1) An incident ray normal to the face BC has direction cosines

$$(l, m, n) = \sin \delta \sin \alpha, \quad \sin \delta \cos \alpha, \quad \cos \delta.$$

It passes straight through to the face AB, whose normal is

$$(\lambda, \mu, \nu) = (0, 1, 0).$$

The angle of incidence θ is given by $\cos \theta = l\lambda + m\mu + n\nu = \sin \delta \cos \alpha$, and the reflected ray is

$$l' = 2\lambda \cos \theta - l = - \sin \delta \sin \alpha,$$
$$m' = \sin \delta \cos \alpha, \qquad n' = - \cos \delta.$$

(2) This strikes AC, whose normal is $(\lambda, \mu, \nu) = (\sin \beta, \cos \beta, 0)$, the angle of incidence being θ', where

$$\cos \theta' = l'\lambda + m'\mu + n'\nu = \sin \delta \sin \alpha \sin \beta + \sin \delta \cos \alpha \cos \beta$$
$$= \sin \delta \cos (\alpha - \beta),$$

and the reflected ray is

$$l'' = 2\lambda \cos \theta' - l' = \sin \delta \sin (\alpha - 2\beta)$$
$$m'' = \sin \delta \cos (\alpha - 2\beta), \qquad n'' = \cos \delta.$$

on reduction.

(3) This ray strikes BC, with $(\lambda, \mu, \nu) = (\sin \delta \sin \alpha, \sin \delta \cos \alpha, \cos \delta)$ at an angle θ'', where

$$\cos \theta'' = l'' \lambda + m''\mu + n''\nu = \sin^2 \delta \cos 2\beta + \cos^2 \delta$$

on reduction, and the reflected ray becomes in the same way

$$l''' = 2 \sin \alpha \sin \delta \,\{\sin^2 \delta \cos 2\beta + \cos^2 \delta\} - \sin \delta \sin (\alpha - 2\beta)$$
$$m''' = 2 \cos \alpha \sin \delta \,\{\sin^2 \delta \cos 2\beta + \cos^2 \delta\} - \sin \delta \cos (\alpha - 2\beta)$$
$$n''' = 2 \cos \delta \,\{\sin^2 \delta \cos 2\beta + \cos^2 \delta\} - \cos \delta.$$

(4) This ray is incident on AC, with normal ($-\sin\beta$, $\cos\beta$, 0) at an angle θ''', where

$$\cos\theta''' = 2\sin\delta\cos(\alpha+\beta)\{\sin^2\delta\cos 2\beta+\cos^2\delta\} - \sin\delta\cos(\alpha-\beta),$$

and gives a reflected ray, on reduction,

$$l^{iv} = \sin\alpha\sin\delta - 2\sin\delta\sin(\alpha+2\beta)\{\sin^2\delta\cos 2\beta+\cos^2\delta\}$$
$$m^{iv} = -\cos\alpha\sin\delta + 2\sin\delta\cos(\alpha+2\beta)\{\sin^2\delta\cos 2\beta+\cos^2\delta\}$$
$$n^{iv} = \cos\delta - 2\cos\delta\{\sin^2\delta\cos 2\beta+\cos^2\delta\}.$$

(5) There is a final reflection on AB, after which the ray becomes

$$l^{v} = -\sin\alpha\sin\delta + 2\sin\delta\sin(\alpha+2\beta)\{\sin^2\delta\cos 2\beta+\cos^2\delta\}$$
$$m^{v} = -\cos\alpha\sin\delta + 2\sin\delta\cos(\alpha+2\beta)\{\sin^2\delta\cos 2\beta+\cos^2\delta\}$$
$$n^{v} = -\cos\delta + 2\cos\delta\{\sin^2\delta\cos 2\beta+\cos^2\delta\}.$$

The angle of incidence on the surface BC, through which it is now refracted, is ϕ, where

$$\cos\phi = l^{v}\sin\alpha\sin\delta + m^{v}\cos\alpha\sin\delta + n^{v}\cos\delta,$$

which may be reduced to

$$-\cos\phi = 1-2\{\cos^2\delta+\sin^2\delta\cos 2\beta\}^2.$$

The angle ϕ is the divergence from the original path just before emergence, and it has an important property, not generally realised, which does not occur in the next problem we investigate. The final divergence in this particular application is independent of the other angles (B and C) of the prism, whether they be 45° or not, and is solely determined by the vertical and dihedral angles.

Now let $\beta = 90° + \varepsilon$, $\delta = 90° + \eta$,

and therefore

$$-\cos\phi = 1 - 2\{\sin^2\eta - \cos^2\eta\cos 2\varepsilon\}^2$$
$$\cos\phi/2 = -\sin^2\eta + \cos^2\eta\,(1 - 2\sin^2\varepsilon);$$

or, for small values, retaining squares only of small quantities,

$$1-\tfrac{1}{2}\cdot\phi^2/4 = -\eta^2 + (1-2\epsilon^2)(1-\eta^2)$$
$$= 1 - 2\varepsilon^2 - 2\eta^2,$$

or

$$\phi = 4\sqrt{\epsilon^2+\eta^2}.$$

The final refraction multiplies this by the index n of the prism, giving the result quoted in the introduction.

The degree of independence of the two effects may be investigated readily. If the trace, on the plane xy, of the final ray before emergence, makes an angle ψ with AB, $\tan\psi = m^{v}/l^{v}$.

The inclination to AB of the normal is ψ' where $\tan\psi' = \cot\alpha$. Thus, for the inclination of the trace to the normal,

$$\tan(\psi - \psi') = \left(\frac{m^{\text{v}}}{l^{\text{v}}} - \cot\alpha\right)\Big/\left(1 + \frac{m^{\text{v}}}{l^{\text{v}}}\cot\alpha\right)$$

$$= \frac{m^{\text{v}}\sin\alpha - l^{\text{v}}\cos\alpha}{l^{\text{v}}\sin\alpha + m^{\text{v}}\cos\alpha}$$

$$= \frac{2\sin 2\beta\,(\sin^2\delta\cos 2\beta + \cos^2\delta)}{1 - 2\cos 2\beta\,(\sin^2\delta\cos 2\beta + \cos^2\delta)}.$$

This is again independent of the angles B and C of the prism, so that the partial deviations, in and perpendicular to the plane ABC, share the property of the whole deviation.

Writing $\delta = 90° + \eta$, $\beta = 90° + \varepsilon$, and expanding in terms of the small quantities η and ε, the partial deviation is found to be

$$\psi - \psi' = 4\varepsilon\,(1 + 2\eta^2 + 16/3\varepsilon^2)$$

in the plane ABC. Here η only enters to the *third* order of small quantities and in no practical case can affect this partial deviation to a measurable extent. The same remark applies to the effect of ϵ on the deviation perpendicular to the plane ABC.

The two effects can therefore be treated quite separately in all practical cases. Even if one of the errors were as much as 5°, its neglect while estimating the other would only introduce a discrepancy of $(5\pi/180)^2$ compared with unity, or not exceeding 0·7 per cent.

We may finally suppose the effects of prism error to be 4ε and 4η in perpendicular planes before emergence, and therefore $4n\varepsilon$, $4n\eta$ after emergence. These are the formulæ quoted, and the analysis of the method is now complete.

The Second Method.

A method which has been used erroneously is now treated briefly. The path of a ray is shown in fig. 3.

The axes and direction cosines of the normals are as before. The incident ray strikes AB normally, in the direction (0, 1, 0), and is incident on BC whose normal is $(\lambda, \mu, \nu) = (\sin\delta\sin\alpha, \sin\delta\cos\alpha, \cos\delta)$ at an angle θ, where $\cos\theta = \sin\delta\cos\alpha$.

The reflected ray is, by a calculation just like those preceding,

$$l' = 2\sin^2\delta\sin\alpha\cos\alpha$$

$$m' = 2\sin^2\delta\cos^2\alpha - 1$$

$$n' = 2\sin\delta\cos\delta\cos\alpha.$$

This ray now falls on AC, whose normal is $(-\sin\beta, \cos\beta, 0)$, at an angle of incidence θ', where

$$\cos\theta' = -l'\sin\beta + m'\cos\beta = -\cos\beta + 2\sin^2\delta\cos\alpha\,(\cos\alpha\cos\beta - \sin\alpha\sin\beta)$$

$$= -\cos\beta + 2\sin^2\delta\cos\alpha\cos(\alpha+\beta).$$

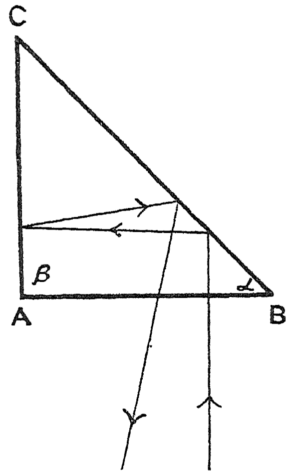


FIG. 3.

It is reflected as a ray in direction (l'', m'', n'') where

$$l'' = -2\sin^2\delta\cos\alpha\sin(\alpha+2\beta) + \sin^2\beta$$

$$m'' = 2\sin^2\delta\cos\alpha\cos(\alpha+2\beta) - \cos^2\beta$$

$$n'' = -2\sin\delta\cos\delta\cos\alpha,$$

and this ray is then incident on BC. Its final direction before emergence is (l''', m''', n''') where

$$l''' = 2\sin^4\delta\sin 2\alpha\cos(2\alpha+2\beta) - 2\sin^2\delta\cos^2\delta\sin 2\alpha - \sin 2\beta\cos 2\delta$$

$$m''' = 4\sin^4\delta\cos^2\alpha\cos(2\alpha+2\beta) - 4\sin^2\delta\cos\alpha\cos(\alpha+2\beta) - 4\sin^2\delta\cos^2\delta\cos^2\alpha + \cos^2\beta$$

$$n''' = 4\sin^3\delta\cos\delta\cos\alpha\cos(2\alpha+2\beta) - 2\sin\delta\cos\delta\cos(\alpha+2\beta) + 2\sin\delta\cos\delta\cos\alpha\,(1-2\cos^2\delta).$$

The cosine of the angle of incidence on AB before refraction is m'''. These expressions are in general complicated, but their implications can be determined by special cases. Suppose, for example, that there is no pyramidal error. Then $\delta = 90°$, and we find

$$n''' = 0, \qquad l''' = \sin(4\alpha+2\beta), \qquad m''' = \cos(4\alpha+2\beta).$$

If γ is the angle at C, $2\alpha+2\beta = 180°-2\gamma$ in all cases, and therefore the final deviation after emergence is easily seen to be in the plane ABC, and equal to *twice the difference of the angles at* B *and* C multiplied by n.

This method can give no information regarding the angular error. It would give no angular error, whatever the magnitude of A, provided B and C were equal. An elementary figure at once shows that a ray incident on AB normally will strike AC normally and retrace its path if $B = C$. We have, in fact, merely verified that the general formulæ are true in a special case. Suppose now that B and C are exactly equal to 45°, we then find

$$l''' = -2 \sin^2 \delta \cos^2 \delta$$

$$m''' = -1 + 2 \sin^2 \delta - 2 \sin^2 \delta \cos^2 \delta = -1 + 2 \sin^4 \delta$$

$$n''' = 2\sqrt{2} \sin^3 \delta \cos \delta,$$

which may be verified by the fact that the sum of their squares is unity. To a sufficient order of small quantities, with $\delta = 90° + \eta$, we may show that these are equivalent to

$$l''' = 0, \qquad m''' = \cos (2\eta \sqrt{2}), \qquad n''' = -\sin (2\eta \sqrt{2}),$$

representing a ray perpendicular to AB, with an internal angle of incidence $2\eta\sqrt{2}$. The final deviation is therefore $2n\eta\sqrt{2}$, and it is perpendicular to that caused by inequality of the angles B and C. It does not appear to be necessary to give a proof again, for this case, of the independence to a sufficient order of the two sources of deviation. The final conclusion regarding this method is, that the two displacements of image from object in the focal plane of a combination of focal length f are

$$2nf\,(\beta \sim \gamma) \qquad \text{and} \qquad 2n\eta \sqrt{2}f$$

where β and γ are the angles B and C of the prism and η is the pyramidal error. The method can obviously, with this new formula, be used to determine pyramidal error, but not angular error, though it is less sensitive. The relative displacements of the image in the first and second methods are in the ratio $4/2\sqrt{2}$ or $\sqrt{2}$, practically 1–5. This ratio has been confirmed in the laboratory with many prisms containing pyramidal error by Prof. Cheshire.

A New Method of Determining Fundamental Errors.

In the present section, we put forward a method of determination of pyramidal error which is free from any complication due to necessity for exact preliminary setting of the apparatus, in order to distinguish the effect of angular error. The analysis of the method is a little tedious when carried out fully,

but the final formula and the experimental arrangement are remarkably simple.

The principle of the method again involves the measurement of a displacement of an image formed in the focal plane of a receiving system, but the two perpendicular directions of displacement are indicated automatically by the apparatus without preliminary setting. The actual point used is displaced solely by the pyramidal error, in the estimation of this particular effect.

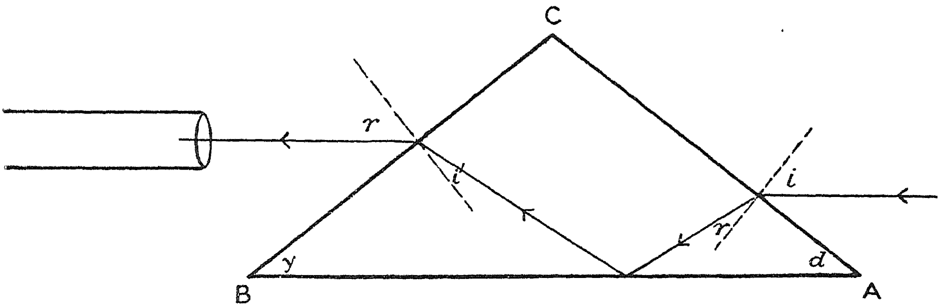


FIG. 4.

The prism is arranged as in the figure, on a horizontal table, and parallel light is incident. The path of one ray is shown, and, so far as angular error is concerned, we shall see later that the magnitude of the "right angle" is not relevant, but only the values of α and γ. For the case in which they are equal, and pyramidal error is absent, the light obviously emerges parallel to its original direction, and is focussed to a definite point by the receiving system. This point is identical with that obtained when the prism is removed, and we shall call it the "centre" of the focal plane.

If the prism be now rotated about the vertical in either direction, this point moves in the focal plane and traces out a definite curve. We must, in the first place, investigate the nature of this curve when there is no pyramidal error: (1) with the angle γ nearer to the receiver, (2) with the prism reversed and α nearer to the receiver. The angles α and γ may be supposed only slightly different, and we shall show that the curves (1) and (2) are of identical shape, consisting of either parabolas or semi-cubic parabolas lying parallel, with their vertices in line with the "centre" of the focal plane. Afterwards we show that when pyramidal error is present, the vertices of the curves are displaced in the perpendicular direction to an equal extent in opposite senses in cases (1) and (2), and that the interval between the vertices of the two curves then obtained affords a simple measure of the pyramidal error. The fundamental principle of the method is that, when only angular error is present,

the vertices of the curves obtained by rotating the prism are in a vertical line with the focus of the light when the prism is absent, and the light incident directly on the receiver, whereas pyramidal error displaces them in the perpendicular direction.

Consider now the nature of the curves when pyramidal error is absent.

Let the prism be twisted round the vertical through a small angle ϕ from its position of "normal" adjustment, in which rays go through principal planes and are focussed at the centre of the focal plane. AB, in normal adjustment, is the axis of x, that of z is vertical, and of y perpendicular to the paper. After the rotation ϕ, the normal to the face represented by AC, on which light is incident, has direction cosines

$$\sin\alpha\cos\phi, \qquad \sin\alpha\sin\phi, \qquad -\cos\alpha,$$

and the incident light is in the direction (1, 0, 0), the axis of x. The angle of incidence ι is given by $\cos\iota = \sin\alpha\cos\phi$, and the angle of refraction r is given by

$$n\sin r = \sin\iota/\delta = \delta\sqrt{(1-\sin^2\alpha+\sin^2\alpha\sin^2\phi)},$$

n being the index of the prism.

We shall require a theorem regarding the direction cosines of a refracted ray, which, although practically essential for this type of problem, is not contained in current text-books. A proof is not appended. The theorem states that if a ray falls in the direction (l, m, n) on a surface whose normal is (λ, μ, ν), the direction of the refracted ray is (l', m', n') where

$$l' = \lambda\cos\iota\left(\frac{\cos r}{\cos\iota} - \frac{\sin r}{\sin\iota}\right) + l\frac{\sin r}{\sin\iota}$$

$$m' = \mu\cos\iota\left(\frac{\cos r}{\cos\iota} - \frac{\sin r}{\sin\iota}\right) + m\frac{\sin r}{\sin\iota}$$

$$n' = \nu\cos\iota\left(\frac{\cos r}{\cos\iota} - \frac{\sin r}{\sin\iota}\right) + n\frac{\sin r}{\sin\iota}$$

ι and r being the angles of incidence and refraction.

Applying this theorem, the refracted ray in the present problem becomes

$$l' = \sin\alpha\cos\phi\,(\cos r - \cos\iota/n) + 1/n$$

$$m' = \sin\alpha\sin\phi\,(\cos r - \cos\iota/n)$$

$$n' = -\cos\alpha\,(\cos r - \cos\iota/n).$$

On reflection at the surface AB, the ray becomes

$$l'' = \sin\alpha\cos\phi\,(\cos r - \cos\iota/n) + 1/n$$
$$m'' = \sin\alpha\sin\phi\,(\cos r - \cos\iota/n)$$
$$n'' = \cos\alpha\,(\cos r - \cos\iota/n)$$

when measured outwards from the surface BC. The normal to this surface, measured outwards, is $(\sin\gamma\cos\phi, \sin\gamma\sin\phi, \cos\gamma)$, and the new angle ι' of incidence is given by

$$\cos\iota' = l''\sin\gamma\cos\phi + m''\sin\gamma\sin\phi + n''\cos\gamma.$$

If (l''', m''', n''') is the final direction after refraction,

$$m''' = \sin\gamma\sin\phi\,\{\cos r' - n\cos\iota'\} + n\,.\,m'',$$
$$n''' = \cos\gamma\,\{\cos r' - n\cos\iota'\} + n\,.\,n''.$$

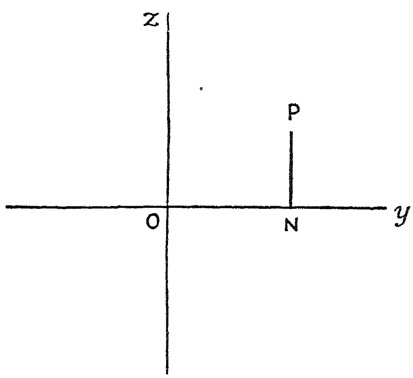


FIG. 5.

In fig. 5, let the paper represent the focal plane of the receiver, of focal length f, and let O be the *centre* of the plane, as already defined. Then the ray is focussed to a point P, where

$$y = \mathrm{ON} = fm'''$$
$$z = \mathrm{NP} = fn'''.$$

By determining m''', n''' in terms of the small angle ϕ, the locus of P may be found by elimination of the variable ϕ. We shall expand the functions concerned, in powers of ϕ, and retain only leading powers, for the variation of ϕ, within the range of vision of the receiver, will be very small. These

expansions are somewhat tedious, and only the main steps in the reduction are quoted. We find, neglecting ϕ^4,

$$\cos\iota = \sin\alpha\left(1-\frac{\phi^2}{2}\right),\quad \cos r = \frac{1}{\mu}(n^2-\cos^2\alpha)^{\frac{1}{2}}\left\{1-\frac{\phi^2\sin^2\alpha}{2(n^2-\cos^2\alpha)}\right\}$$

$$nl'' = \cos^2\alpha+\sin\alpha\,(n^2-\cos^2\alpha)^{\frac{1}{2}}$$

$$+\frac{\phi^2\sin\alpha}{2(n^2-\cos^2\alpha)^{\frac{1}{2}}}\{\cos 2\alpha-n^2+2\sin\alpha\,(n^2-\cos^2\alpha)^{\frac{1}{2}}\}$$

$$nm'' = \phi\sin\alpha\,\{(n^2-\cos^2\alpha)^{\frac{1}{2}}-\sin\alpha\}$$

$$+\frac{\phi^3}{6}\sin\alpha\left\{4\sin\alpha-(n^2-\cos^2\alpha)-\frac{3\sin\alpha}{(n^2-\cos^2\alpha)^{\frac{1}{2}}}\right\}$$

$$nn'' = \cos\alpha\,\{-\sin\alpha+(n^2-\cos^2\alpha)^{\frac{1}{2}}\}$$

$$+\frac{\phi^2\cos\alpha}{2}\left\{\sin\alpha-\frac{\sin^2\alpha}{(n^2-\cos^2\alpha)^{\frac{1}{2}}}\right\}$$

$$n\cos\iota' = \cos(\gamma-\alpha)\,(n^2-\cos^2\alpha)^{\frac{1}{2}}+\cos\alpha\sin(\gamma-\alpha)-\frac{\phi^2(1-n^2)}{2(n^2-\cos^2\alpha)^{\frac{1}{2}}}.$$

In this last formula we have put $\gamma=\alpha=45^\circ$ in the terms involving ϕ^2, for the error introduced is of a higher order than ϕ^2, and, moreover, cannot alter the vertex of the curve, which corresponds to $\phi=0$.

We notice that $\iota'=r$, as it should do, if $\gamma=\alpha$.

It is convenient to write ε for $\gamma-\alpha$ subsequently.

Continuing the approximation,

$$\cos^2 r' = 1-n^2+n^2\cos^2\iota'$$

$$=\sin^2\alpha+2\varepsilon\cos\alpha\,(n^2-\cos^2\alpha)^{\frac{1}{2}}-\phi^2(1-n^2)$$

retaining ε only to the first power. Thus to the same order,

$$\cos r' = \sin\alpha+\varepsilon\cot\alpha\,(n^2-\cos^2\alpha)^{\frac{1}{2}}-\frac{\phi^2}{2\sin\alpha}(1-n^2).$$

The term independent of ϕ in m''' is, to order ε,

$$\sin\gamma\,\{\sin\alpha-\varepsilon\cos\alpha-(n^2-\cos^2\alpha)^{\frac{1}{2}}+\varepsilon\cot\alpha\,(n^2-\cos^2\alpha)^{\frac{1}{2}}\}$$

$$+\sin\alpha\,\{(n^2-\cos^2\alpha)^{\frac{1}{2}}-\sin\alpha\}$$

or

$$[\varepsilon\cos\alpha\sin\gamma-(\sin\gamma-\sin\alpha)]\,[(n^2-\cos^2\alpha)^{\frac{1}{2}}-\sin\alpha].$$

The first factor is easily shown to be of order ε^2, which will in practice be incapable of detection. The leading term in m'' is therefore that in ϕ^3, whose coefficient is easily shown not to be small when $\gamma=\alpha$. Thus $m'''=a\phi^3$ is

the form of m''', for small rotations, and the form is precisely the same if the prism is reversed so as to interchange α and γ.

We now consider n'''.

$$n''' = \cos\gamma\,(\cos r' - n\cos\iota') + n\,.\,n'',$$

and the portion independent of ϕ is found to be

$$[(\cos\gamma - \cos\alpha) - \varepsilon\cot\alpha\cos\gamma]\,[\sin\alpha - (n^2 - \cos^2\alpha)^{\frac{1}{2}}].$$

The first factor is equal to

$$2\sin\frac{\gamma+\alpha}{2}\sin\frac{\alpha-\gamma}{2} - \varepsilon\cot\alpha\cos\gamma = -\epsilon\sqrt{2}$$

to the first order of ε. The value of n''' when $\phi = 0$ is therefore

$$-\epsilon\sqrt{2}\left\{\frac{1}{\sqrt{2}} - \left(n^2 - \frac{1}{2}\right)^{\frac{1}{2}}\right\} = +\varepsilon\{\sqrt{2n^2-1} - 1\} = b \text{ (say)}.$$

There is no term in ϕ, and the coefficient of ϕ^2 in n''' is found to be

$$(2n^2 - 1)\left(1 - \frac{1}{\sqrt{2n^2-1}}\right),$$

which is positive. If it be called c, we have

$$\begin{aligned} n''' &= b + c\phi^2 \\ m''' &= a\phi^3. \end{aligned}$$

The equation of the curve obtained in the focal plane by rotating the prism is therefore

$$a^2(z - b)^3 = c^3y^2,$$

which is a semicubic parabola with its vertex at the point $z = b$, $y = 0$.

When the prism is reversed, a and c are not altered, but b, which is proportional to $\gamma - \alpha = \epsilon$, changes sign, and we obtain the same parabola shifted a distance $2b$ vertically. The " centre " of the plane is vertically midway between the cusps. The two curves are shown in fig. 6, where O is the " centre."

The cusp which occurs when the rays pass through principal planes is peculiarly convenient for measurement. If the prism is slowly rotated, the image traverses the cusp, and the motion can be stopped exactly when it reaches the cusp. These cusps would become less sharp if $\alpha - \gamma$ were so large that the square became appreciable, for m''' would then contain a term proportional to ϕ. This can hardly occur, however, in a prism designed to have angles of 45°.

If Q, Q′ are the vertices, $OQ = OQ' = \varepsilon\,(\sqrt{2n^2-1} - 1)$ where ϵ is the difference of angle in the prism, which can thus be determined at once. Since the prism is properly adjusted when the cusp is determined, the adjustment, in a sense,

is automatic, and its accuracy is tested by reversing the prism and showing that Q′, O, Q are in a straight line and equidistant.

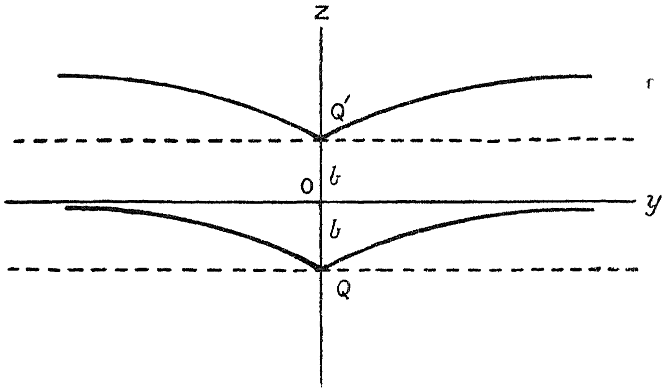


FIG. 6.

The simplicity of this method justifies the somewhat lengthy discussion which we have found necessary in order to establish its validity.

Elementary Treatment.

If our object were merely to determine the vertex of a curve, and not to demonstrate and determine its shape, the following simple treatment would suffice.

In the figure, the first angle of incidence—in a principal plane, as there is no pyramidal error—is $90°—\alpha$. Thus $\sin \iota = \cos \alpha$, $\sin r = \cos \alpha/n$.

If θ is the inclination of the third part of the ray to AB, $\theta = 90—\alpha—r$, and therefore

$$\iota' = 90 - \gamma - \theta = r + (\alpha-\gamma)$$

$$\sin \iota' = \sin (r + \alpha - \gamma) = \sin r + (\alpha - \gamma) \cos r,$$

since $\alpha - \gamma$ is small and its square is negligible. Thus

$$\sin r' = n \sin \iota' = n \sin r + n(\alpha-\gamma) \cos r$$

$$= \cos \alpha + (\alpha-\gamma) \sqrt{n^2 - \cos^2 \alpha}.$$

If $r' = 90 - \alpha + u$, where u is small,

$$\cos \alpha + \sin \alpha \, u = \cos \alpha + (\alpha - \gamma) \sqrt{n^2 - \cos^2 \alpha}$$

or

$$u = (\alpha - \gamma) \sqrt{n^2 - \cos^2 \alpha}/\sin \alpha = (\alpha - \gamma) \sqrt{2n^2 - 1}.$$

The slope of the emergent ray to the horizontal—its position in the absence of the prism—is, if $\varepsilon = \gamma - \alpha$,

$$\begin{aligned} 90 - \gamma - (90 - \alpha + u) &= \alpha - \gamma - u \\ &= (\alpha - \gamma)\{1 - \sqrt{2n^2 - 1}\} \\ &= \varepsilon\{\sqrt{2n^2 - 1} - 1\}, \end{aligned}$$

and the displacement of the image is $f\varepsilon\{\sqrt{2n^2 - 1} - 1\}$ as before, in the vertical direction. When the prism is reversed, α and γ are interchanged, and the displacement changes sign through the factor ε.

The Pyramidal Error.

General considerations, combined with the preceding investigation on the superposition of the two errors, readily show that the presence of pyramidal error will have no appreciable effect on the general shape of the curves, and can only alter the positions of their vertices. In determining its effect, therefore, on theoretical grounds, it is not necessary to examine the result of a rotation of the prism, and we may suppose the line AB in the figure is rigorously parallel to the incident light along the axis of x. This is sufficient to determine the new vertices of the curves.

The plane end ABC will not now be vertical, but inclined to the vertical at a small angle η—the pyramidal error—and the upper edge through C is still perpendicular to this plane. This edge has direction cosines $(0, \cos\eta, \pm \sin\eta)$, being perpendicular to the x-axis and at η to the y-axis. The sign of the ambiguity depends on its two possible directions of slope, or the sign of η. As the prism will ultimately be reversed—equivalent to a change of sign of η—we may choose either, and we select $(0, \cos\eta, -\sin\eta)$. The direction cosines of AB are $(\cos\alpha, \sin\alpha\sin\eta, \sin\alpha\cos\eta)$, for it is perpendicular to this edge, and at an angle α to the x-axis. The normal to the face represented by AB is perpendicular to the edge and to AB, and becomes

$$(+\sin\alpha, \; -\cos\alpha\sin\eta, \; -\cos\alpha\cos\eta)$$

when measured into the prism from AB. The normal to the face represented by BC is similarly

$$\sin\gamma, \quad \cos\gamma\sin\eta, \quad \cos\gamma\cos\eta$$

when measured out of the prism.

The initial ray along (1, 0, 0) has an angle of incidence ι given by $\cos\iota = \sin\alpha$, or $\iota = 90^\circ - \alpha$. Thus $\sin r = \cos\alpha/n$, and the refracted ray is

$$l' = \sin\alpha\,\{\cos r - \cos\iota/n\} + 1/n = \sin\alpha/n\,\{\sqrt{n^2-\cos^2\alpha} - \sin\alpha\} + 1/n$$
$$m' = -\cos\alpha\sin\eta\,(\cos r - \cos\iota/n) = -1/n\cos\alpha\sin\eta\,\{\sqrt{n^2-\cos^2\alpha} - \sin\alpha\}$$
$$n' = -\cos\alpha\cos\eta\,\{\cos r - \cos\iota/n\} = -1/n\cos\alpha\cos\eta\,\{\sqrt{n^2-\cos^2\alpha} - \sin\alpha\}.$$

After internal reflection at the face of trace AB, we may take the on-going ray as (l'', m'', n''), where

$$l'' = 1/n\,(\cos^2\alpha + \sqrt{n^2-\cos^2\alpha\sin\alpha})$$
$$m'' = -1/n\cos\alpha\sin\eta\,(\sqrt{n^2-\cos^2\alpha} - \sin\alpha)$$
$$n'' = 1/n\cos\alpha\cos\eta\,(\sqrt{n^2-\cos^2\alpha} - \sin\alpha).$$

If ι' is the new angle of incidence on the face BC

$$\cos\iota' = l''\sin\gamma + m''\cos\gamma\sin\eta + n''\cos\gamma\cos\eta,$$

and we see that ι' is independent of η, and has the value for $\eta = 0$, neglecting η^2.

If $\alpha = \gamma$, this value is r, or $\sin^{-1}(\cos\alpha/n)$, and $r' = 90^\circ - \alpha$.

The refracted or final ray then becomes (l''', m''', n''') where

$$m''' = \cos\gamma\sin\eta\,(\cos r' - n\cos\iota') + n\,m''$$
$$= [\sin\alpha - (n^2-\cos^2\alpha)^{\frac{1}{2}}](\cos\alpha + \cos\gamma)\sin\eta$$
$$= -\eta\{\sqrt{2n^2-1} - 1\}$$

since η is small. Moreover,

$$n''' = \cos\gamma\cos\eta\,(\cos r' - n\cos\iota') + n\,.\,n'' = 0.$$

Accordingly, there *is no vertical displacement* of the vertex of a curve due to pyramidal error, and the horizontal displacement is

$$f\eta\,\{\sqrt{2n^2-1} - 1\}.$$

This is on the other side of the vertical if the prism is reversed.

The final results are shown in the figure (fig. 7).

O is the "centre" of the focal plane, or position of the image when the prism is removed.

(1) and (1′) are the curves obtained from a prism without pyramidal error, but with inequality of base angles.

(2) and (2′) are obtained with a prism with pyramidal error only.

(3) and (3′) are given by a prism with both types of error. They may, alternatively, be at P and Q in the figure.

It is not difficult to secure equality of base angles in a prism even when angular error is present in the "right angle." The vertical distances OB are therefore usually very small.

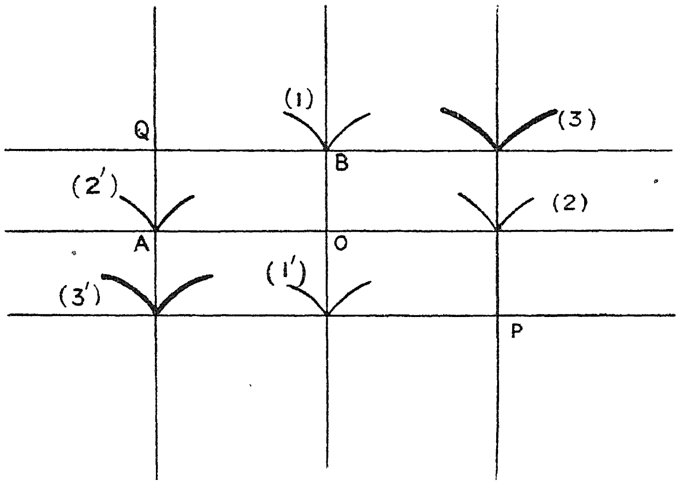


FIG. 7.

The distances in the figure are, if f is the focal length of the receiver,

$$OA = f\eta\ \{\sqrt{2n^2 - 1}\ -1\}$$

$$OB = f\epsilon\ \{\sqrt{2n^2 - 1}\ -1\}$$

where η is the pyramidal error, and ϵ the difference of base angles. The receiver can be set with vertical—or perpendicular to the table—cross wires permanently.

*Some Experiments on the Proportionality of Mass and Weight.**

By Harold H. Potter, B.Sc., 1851 Exhibition Scholar, King's College, London.

(Communicated by Prof. O. W. Richardson, F.R.S. Received July 3, 1923.)

The earliest experiments on this subject were carried out by Newton, who came to the conclusion that the gravitational accelerations of gold, silver, lead, glass, sand, common salt, wood, water and wheat were equal to within one part in a thousand. In 1827, similar experiments were carried out by Bessel.† His method was to suspend his pendulum bob from two threads of different length and to measure the period in each case by comparison with a standard clock. The difference in length of the two threads being known, Bessel was able to calculate the length of the "simple pendulum which beats a second." His experiments were carried out with great care, and Bessel came to the conclusion that, with one possible exception—the case of water—the gravitational acceleration was the same for all substances which he tried to one part in 60,000.

Bessel endeavoured to explain the difference which he had found in the case of water by assuming that the water acquired a velocity relative to the containing vessel, on account of the difference of the centrifugal force at various points in the liquid. M. Lubeck has shown that Bessel's explanation is not the correct one, and himself offers an explanation which is hardly satisfactory.

Prof. O. W. Richardson‡ has suggested a theory which might lead one to expect some such variation for water and for several other light elements and compounds.

The mass of an atom is due almost entirely to its nucleus, and it is highly probable that the nuclei of all elements are formed by the close union of either hydrogen or helium nuclei, or both. Experiments in radio-activity have shown beyond all doubt the presence of helium in the nuclei of the elements of high atomic weight, and Rutherford has apparently been successful in driving hydrogen out of the nitrogen atom. It is highly probable that the helium nucleus itself is built up of four hydrogen nuclei; and if that is so, we

* This paper is considerably condensed from a manuscript in the archives of the Society.

† 'Mémoires Relatifs à la Pendule,' vols. 4 and 5.

‡ Richardson, 'Electron Theory of Matter,' 1st edit., p. 592 (1914); *cf.* also Richardson, 'Phys. Rev.,' vol. 31, pp. 609, 710 (1910), and 'Phil. Mag.,' vol. 53, p. 138 (1922).

have an explanation of the constancy of the ratio of mass to weight for various substances, in so far as we are dealing in all cases with one substance—hydrogen. It is most probable, at any rate, that we have not more than two fundamental positive ions—the nuclei of hydrogen and helium. This view has been greatly strengthened in recent years by the positive-ray researches of F. W. Aston. The close approximation of the atomic weights to whole numbers has been noted by many writers, but the work of Aston has made this point much more noteworthy, inasmuch as he has shown that in those cases where the atomic weights are not whole numbers, the discrepancies are explained by the presence of isotopes, each of the isotopes having an integer atomic weight. This certainly suggests that the elements are built up of a fundamental unit or units.

Prof. Richardson suggests that there may be a slight difference in the gravitational constants of the helium and the hydrogen nuclei, the reason why no such difference has ever been found lying in the fact that nearly all the substances for which "g" has been measured have been substances which might reasonably be expected to consist almost entirely of helium. The substances whose atomic weights are divisible by four might be considered to be entirely of helium, whereas in other substances the remainder must be attributed to hydrogen.

The possible constitution of the substances tried by Bessel is given below.

Substance.	Molecular Weight.	Possible Constitution.		Percentage of H.
		He nuclei.	H nuclei.	
Fe	56	14	—	—
Zn	65	16	1	1·5
Pb	207	51	3	1·4
Ag	108	27	—	—
Au	197	49	1	0·5
Fe_3O_4	$3\times56+4\times16$	58	—	—
Marble ($CaCO_3$)	$40+12+3\times16$	25	—	—
Clay (say $Al_2\,(Si_2O_5)_3$)	$2\times27+6\times28+15\times16$	114	6	1·3
Quartz ($Si\,O_2$)	$28+2\times16$	15	—	—
H_2O	$2+16$	4	2	11·1

Thus, of these substances, water is the only one with any appreciable hydrogen content, and water is the substance for which Bessel obtained an anomalous result.

Considering its enormous importance, very little work has been done on this subject since the time of Bessel, so that it appeared desirable that more evidence

on these points should be obtained. The advent of the general theory of Relativity made this demand more imperative, as the whole theory is based on the assumption that the gravitational constant is the same for all bodies. (The principle of equivalence affirms the equality of the gravitational and inertial masses.)

Some experiments on this subject were started in 1914 by Mr. R. C. Richards, under the direction of Prof. Richardson, but were abandoned during the war and an entirely fresh start was made in December, 1919. The object of these experiments has not been to obtain greater accuracy than has been obtained hitherto, but to repeat some of the experiments of Bessel, directing special attention to substances having a large hydrogen content. The substances especially favourable to this experiment are ammonium fluoride and paraffin wax, which adopting the arguments used above contain respectively 25 per cent. and 15 per cent. by weight of hydrogen.

Description of Apparatus.

The method used in these experiments was very similar to that adopted by Bessel, except that some simplifications have been introduced on account of the fact that no attempt has been made to measure the absolute value of the gravitational accelerations, a comparison only of the accelerations being attempted. The principle of the experiment has been to compare the period of the experimental pendulum with that of a standard invar pendulum, by means of the method of coincidences.

The experimental pendulum consisted of an agate knife-edge with brass mountings, a fine steel suspension wire and a hollow cylindrical bob which could hold in turn the various substances to be tested.

Knife-Edge Mountings.

The knife and its mountings are shown in figs. 1 and 2. A solid brass cylinder 2 cms. in length and 1 cm. diameter was drilled perpendicular to its

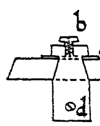


fig 1

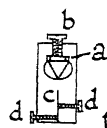


fig 2

axis, so that by the aid of a packing piece (a) and a clamping screw (b) the agate could be securely held in position as shown. The agates were $3 \cdot 5$ cms.

in length. The brass cylinder was drilled with a fine drill along its axis as indicated at (*c*), fig. 2. Into this hole the suspension wire was clamped by means of the side screws (*d d*), figs. 1 and 2.

The Cylinders.

Two types of bob have been used: that used in all the earlier experiments was made by the Cambridge and Paul Scientific Instrument Co. and is shown in fig. 3. It consisted essentially of a hollow brass cylinder with screw-on ends, made as shown, to leave the vessel perfectly cylindrical inside and out. Two adapters screwed into the centres of the two ends, the one carried the suspension wire and the other a thin steel rod terminating in a small steel ball, the use of which will be explained later. The whole was made with great care, the screws being made fairly loose, and all the surfaces of contact between

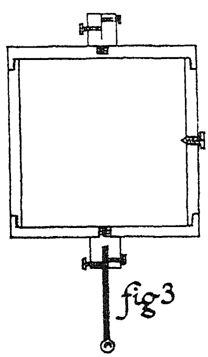


fig 3

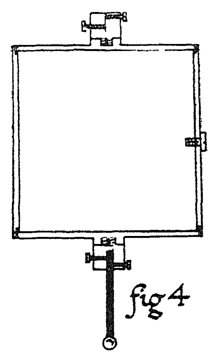


fig 4

the various parts being worked very carefully, so that once the cylinder was taken apart each part would go back again exactly as it was before. The adapters were interchangeable so that the cylinder could be inverted. This is a very essential point, as in filling the cylinder with the various substances under investigation, it was never possible to make the centre of gravity coincide with the centre of figure of the cylinder. By making two observations, the one with the cylinde rone way up and the other with it inverted, it was possible to eliminate this effect.

The type of cylinder shown in fig. 3 was used in all preliminary experiments, but the cylinder was rather heavy, and this became a very serious factor when experimenting on substances such as ammonium fluoride, which have low densities. The screw-on ends had, therefore, to be discarded, owing to the mechanical difficulties involved in turning an accurate screw on a cylinder of 5 cms. diameter, of sufficiently thin material to cause any appreciable

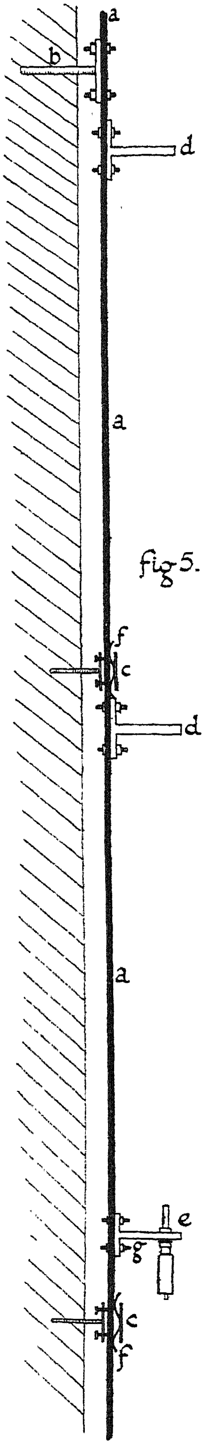


fig 5.

reduction in the weight of the containing vessel. This difficulty was eventually overcome by the use of the type of cylinder shown in fig. 4. The ends were made perfectly flat and each end was fixed to the side by four small screws in the manner shown, the surfaces of contact being ground with great care. Adapters were used as before, but as the ends were only 1 mm. thick, a thicker ring was left at the centre to receive the female screw of the adapter. Two cylinders of this type were used, the first being made entirely of brass, and the second being made with brass ends and adapters but with duralumin sides. In the case of the second cylinder the weight was only 90 gms., and owing to the rapid damping of so light a pendulum it was thought inadvisable to reduce the weight any further. Both cylinders were made by Messrs. Adam Hilger, and so accurately were they worked that they could be taken apart and re-assembled without causing any alteration in the distance between the ends of the adapters of more than 1/200 mm. After some little use, this accuracy was somewhat impaired, but errors due to this cause were never serious and a correction for such errors could be applied in a manner to be described later on.

Mounting of Pendulum.

The mounting of the experimental pendulum is shown in fig. 5. An invar bar (*a*) (*a*) (*a*) 5 cms. wide, 1 cm. thick, and 3 metres long was rigidly bolted to a cast-iron T-piece (*b*) which was cemented into the wall for about 5 ins. Two cast-iron boxes (*c*) (*c*) are shown in further detail in fig. 6. The bar passed through these boxes and was held firmly by steel springs (*f*) (*f*) which forced it back on to the points of three adjusting screws (*h*) (*h*), fig. 6. The boxes were also fitted on either side with an adjusting screw (*k*), fig. 6, which could be used to lightly clamp the bar from the side. The pendulum could be supported from either of two plates (*d*) (*d*), fig. 5, which were firmly bolted to the

invar bar. These plates were carefully ground on their upper face and the agate knife-edge rested directly on the ground surface, the suspension wire passing through a slot cut in the plate (*see* fig. 7).

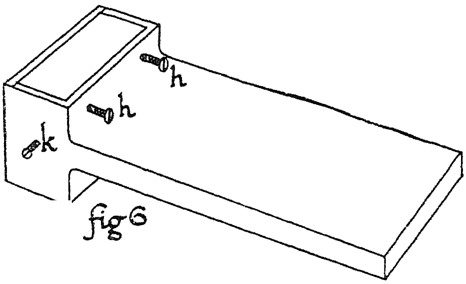


fig 6

Micrometer Measurements.

A Starratt straight micrometer (*e*), fig. 5, with the end highly polished, optically plane and perpendicular to the axis of the micrometer to within 1 min. of arc, was fixed at the lower end of the invar bar. This polishing was undertaken by Messrs. Hilger and the question of perpendicularity was tested by a back reflection method to be described later.

The object of the micrometer was to measure any changes in length of the pendulum, which was so placed on the supports that the steel ball (figs. 3 and 4) hung just above the centre of the polished surface. The contact between the ball and its image in the polished surface was observed under a high-power microscope. The micrometer reading was then taken and so any accidental changes in the length of the pendulum could be detected. This method, which was tested against an electrical one, was found to be most satisfactory, it being possible to read to 1/20,000-in., which was the limit of accuracy of the micrometer. When the pendulum was suspended from the lower of the two plates (*d*) (*d*), fig. 5, the length was 30 ins., so that a change in length of one part in 600,000 could be detected. A sufficiently accurate micrometer in the metric system was unobtainable.

Standard Pendulum.

The standard pendulum was very similar to the "experimental," but the fine steel suspension wire was replaced by an invar rod $\frac{1}{8}$-inch diameter, thus making the pendulum rigid. The bob was of brass, the same size as the bob of the "experimental" pendulum, and the invar rod was secured at the middle of the bob in the manner shown in fig. 8, so that there was no change in length of the standard pendulum due to expansion of the brass. The standard

pendulum had an agate knife-edge and was suspended from a plate similar to that shown in fig. 7, the plate being bolted to an iron girder which was cemented into the wall for some 8 inches.

Southerns* mentions a peculiar effect obtained with invar pendulums, but no such effect has been observed in these experiments, probably owing to the fact that no accurate observations were made until the standard pendulum had been in use for some months, and because only on very rare occasions was there any necessity to move the pendulum on its supports.

The experiments were carried out in the corner of a room in the basement of King's College. The standard pendulum was 6 feet in front of the "experi-

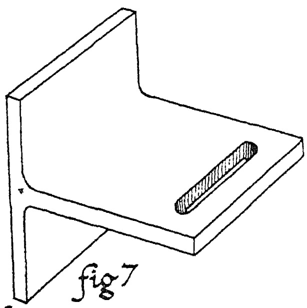


fig 7

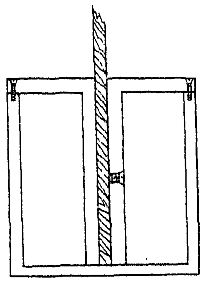


fig 8

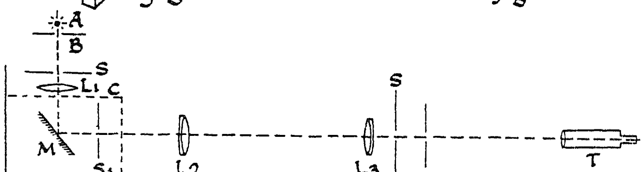


fig 9

mental," and the girders which carried the two pendulums were in different walls, although each was in a main wall of the building.

Both pendulums were entirely cased in, to prevent any trouble arising from air currents. The cases were provided with suitable doors and windows. The microscope passed through a hole in the side of the case of the "experimental" pendulum, and could be withdrawn after the micrometer reading had been taken, so that it did not interfere with the oscillations of the pendulum. The case of the "experimental" pendulum finished on a level with the brass bracket (g), fig. 5, which secured the micrometer to the invar bar. Consequently the scale of the micrometer was outside the case and readings could therefore be made quite easily.

* Southerns, 'Roy. Soc. Proc.,' A, vol. 84, p. 325 (1914).

Arrangements for Measuring Period.

When the "experimental" pendulum was suspended from the lower plate it had very nearly the same period as the standard, but when suspended from the upper plate—the position of the bob remaining the same but the length of the suspension wire being altered—it performed two oscillations to three performed by standard. It is not really necessary, however, in a purely comparative experiment to use two pendulums in the way adopted by Bessel, and the long pendulum was set up merely as a check on the short one. All the results given below refer to the short pendulum, but in a more detailed account of this work which may be found in the Archives of the Royal Society the writer has discussed in detail how, by an extension of the method described below, the periods of two pendulums which are nearly in the ratio of 2 to 3 may be accurately compared.

The period of the "experimental" pendulum has been compared with that of the standard by the method of coincidences. The coincidences have been observed by a method very similar to that adopted by Bessel, but his "cylindre de coincidences" has been replaced by a vane and slit, the vanes being in the plane of oscillation and near the bottom end of the suspension wire. A beam of light was focussed on the slit of the experimental pendulum and an image of this slit was formed on the slit of the standard pendulum. The beam which emerged from the second slit was received in a telescope placed some 6 feet in front of the standard pendulum. The optical system is shown in fig. 9. s_1 s_2 are the vanes and slits of the two pendulums; B a slit illuminated by a source A, L_1 L_2 L_3 are lenses, *s s* two stops, M a plane metal mirror and T the telescope. The case of the "experimental" pendulum is shown by the dotted lines *c c c*.

The mirror M was supported by the invar bar, and serves to turn the beam through a right-angle. This is necessary, as the source and slit could not be placed in the case, partly from lack of room, and partly because of the heat which would be generated. The slit s_1 was at the focus of an achromatic lens L_2 and the slit s_2 was at the focus of another achromatic lens L_3. The slits s_1 s_2 were 1/10 mm. wide, so that in order to get a bright image of s_2 in the telescope it was necessary to obtain sharp focussing and consequently to use good lenses.

The adjustments were made when the pendulums were at rest, and when the pendulums were in motion flashes could be seen in the telescope only when the two pendulums passed through the positions of rest at the same instant. This occurred when the pendulums were in the same phase and when the phases

were exactly opposite, and observations were made in both cases. In dealing with the short pendulum (approximately same period as standard) more than one flash could be seen at each coincidence, but very satisfactory results were obtained by taking the mean time between the first and last flash as the time at which the coincidence occurred.

Calculation of Period.

Let

$T_1 =$ period of experimental pendulum

$T_2 =$ period of standard

$\tau =$ period of coincidence (*i.e.* time taken for pendulums which are in phase to get out of phase and back again).

Then if $T_1 > T_2$

$$T_1 = T_2\left(1 + \frac{T_2}{\tau} + \frac{T_2^2}{\tau^2} + \ldots\right).$$

In practice

$$\tau = 2000 \text{ seconds approx.}$$
$$T_2 = 1\cdot77 \text{ seconds approx.}$$

In order to express T_1 as $T_2 f(\tau)$, it is necessary to know T_2 fairly accurately. T_2 was measured by comparison of the standard pendulum with a standard clock. The period of coincidence was about 15 seconds, but by taking the time required for 100 coincidences a fairly accurate value of T_2 was obtained; it was found to be $1\cdot7703$ seconds.

Thus

$$T_1 = T_2\left(1 + \frac{1\cdot7703}{\tau} + \frac{3\cdot134}{\tau^2}\right).$$

Preliminary Experiments.

The first step in starting these experiments was to obtain a pendulum which under given conditions would always oscillate with the same period. This and the accurate measurement of the period have been all along the most difficult part of the experiment.

Progress was delayed for some time by the peculiar effect which varying amplitude had upon the period of coincidence. Suppose that the standard and experimental pendulums have equal damping coefficients and that the temperature and pressure remain constant throughout the experiment. Then if the pendulums were started at the same time with equal amplitudes their amplitudes would remain equal, and plotting "period of coincidence" against amplitude a straight line fig. 10 (*a*) would be obtained. Now suppose that

the one pendulum was kept with a constant small amplitude while the other pendulum had an amplitude which varied from a large value at the beginning

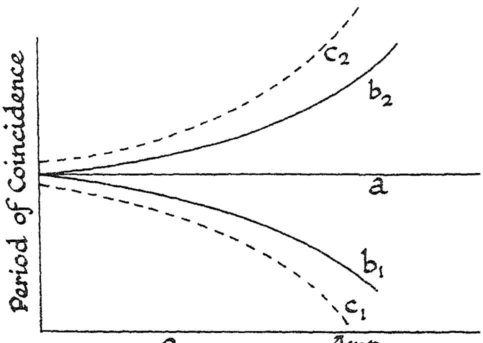


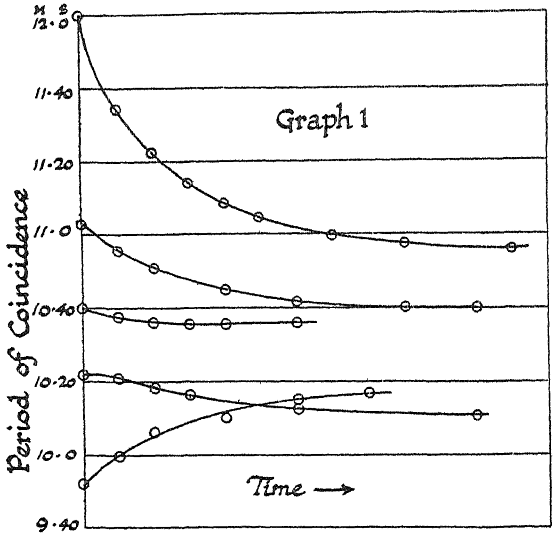
fig 10.

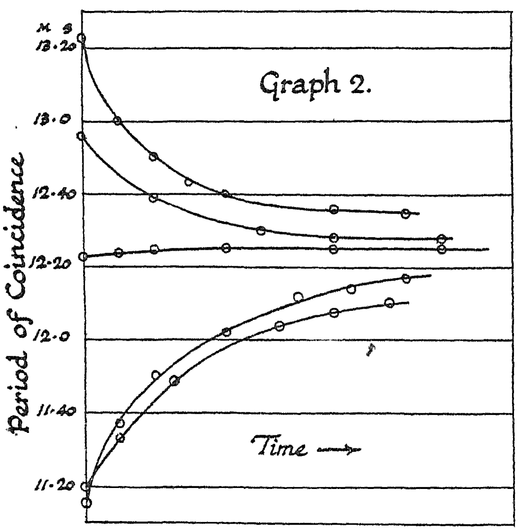
of the experimental to a negligibly small one at the end. Then plotting the amplitude of the latter and the period of coincidence, one of the curves b_1 b_2 should be obtained, b_1 if the quicker pendulum has the constant small amplitude or b_2 for the reverse case. In practice the curve (a) was obtainable, but instead of b_1 and b_2, curves similar to c_1 c_2 were obtained. Thus the amplitude of the pendulums seemed to affect the period to a greater degree than would be expected from theoretical considerations, and, moreover, there was always a residual effect even after the amplitudes had become vanishingly small.

The experiments were carried out with steel knife-edges on a steel plate. The effect appeared to be traceable to the knife-edge, so other methods of suspensions were tried, including strip suspension—the metal strip being clamped in a vice at the top—and the two-point suspension. The strip suspension gave results similar to the knife-edge suspension, whereas other forms of suspension only led to other troubles. The effect was finally got rid of by using knife-edges of agate and steel plates which had been ground to an accuracy of 1/20,000 inch. In previous experiments, the knife-edges and plates had been ground with less care and the effect was evidently due to inequalities in either the knife-edges or the plates. In the case of the strip suspension the effect was probably due to a change in the effective point of suspension as the amplitude decreased.

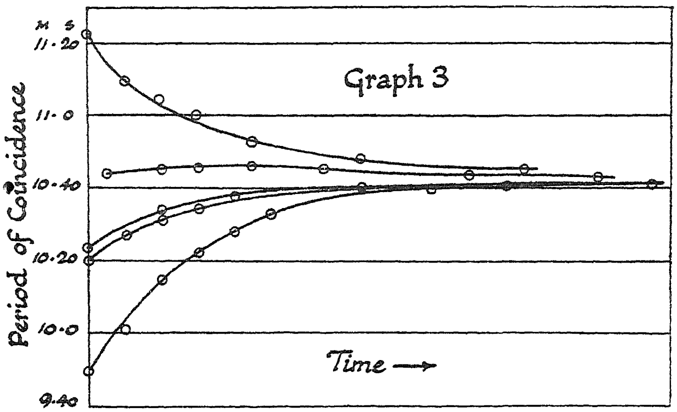
Actual curves showing the effect are shown in graphs 1, 2 and 3. The period of coincidence is plotted as ordinate and the time as abscissæ. The actual shape of the curves depends on the initial amplitudes and the rate of damping, but they should all be asymptotic to one line. Graph 1 is for ordinary hand-sharpened

knife-edges; graph 2 shows curves taken with knife-edges and plates ground to an accuracy of 1/2000 inch, and graph 3 curves taken with agate knife-edges and steel plates each ground to 1/20,000 inch. It will be seen that in graph 3





the curves are all very nearly asymptotic to one line. After grinding to this degree of accuracy the period could be measured to about 1 part in 400,000, and under the same conditions the same value of the period was always found.



Levelling the Supports.

Having obtained a sufficiently accurate method of determining the period, the apparatus was set up in its permanent form. The chief problem in this work was to get the plates (*d*) (*d*), fig. 5, and the polished surface of the micrometer horizontal. This was accomplished by a back-reflection method using an auto-collimating telescope. In the case of the micrometer the whole was immersed in oil, and the images reflected from the polished end of the micrometer and the oil surfaces brought together in the field of view of the auto-collimator. In the case of the plates a trough of oil was placed under the plate and close to it, the reflected image being viewed through the slot in the plate. By placing the telescope half over the slot and half over the polished surface both images could be obtained in the field of view. In the case of both plates and micrometer, rough adjustments were made by using washers under the bolts which secured the plates and micrometer to the invar bar. Fine adjustments were made by means of the screws in the boxes (*c*) (*c*), fig. 5. The screws could be made to impart a slight curvature to the invar bar and so to alter the inclination of the plates. In applying this method it was necessary to level the micrometer, then to level the plate, then the micrometer again, and so on, because in levelling the plate the level of the micrometer surface would be disturbed and *vice versa*. By this method the plates could be levelled to at least $\frac{1}{2}$ min. of arc.

The same method could be applied to tell if the polished surface of the micrometer was perpendicular to the axis. Having once levelled the micrometer surface, all that was necessary was to turn the micrometer and see if the image in the telescope moved.

A high accuracy in the levelling of the plates is required, as otherwise the micrometer readings would depend on the position of the pendulum on the supports. This point was tested by moving the pendulum on its support by the maximum amount permitted by the size of the polished micrometer surface, *i.e.*, all positions for which the steel ball was above any portion of the polished surface. The micrometer reading was found to be absolutely independent of the position of the pendulum. The point was tested again at the end of the series of experiments and was found still to hold good.

Corrections to be applied.

In carrying out an observation it is necessary to know :—

1. Period of coincidence.
2. Approximate period of standard.
3. Dimensions of various parts of apparatus.
4. Weights of various parts of "experimental" pendulum and the total weight of standard.
5. The micrometer readings for each experiment and the temperature at which they were taken.
6. The amplitudes of both pendulums.
7. The temperature and pressure during the experiment.

The measurements of the period of coincidence and the period of the standard have already been discussed.

The dimensions of the apparatus were obtained with a micrometer or a reading microscope, and the weights of the various parts were obtained to 0·0005 grm. on an accurate balance.

The temperature of the experimental pendulum was given by two thermometers placed inside the case, and that of the standard was given by one thermometer. Owing to the low values of the coefficient of expansion of steel and invar—especially the latter—a very accurate knowledge of the temperature was unnecessary. The temperature of the room which was underground was surprisingly constant and could be regulated by means of an electric stove. The pressure was given by a Fortin's barometer.

The amplitudes were given by a mirror scale placed just behind each pendulum and just above the top of the bob, the distance of each scale from the point of suspension of the pendulum being known.

The corrections which have to be made are as follows :—

1. Reduction to Simple Pendulum.
2. Amplitude.
3. Buoyancy—including temperature and pressure corrections.
4. Effect of damping on period.
5. Changes in total length—indicated by micrometer.
6. Non-rigidity of connections between bob and suspension wire and between suspension wire and mountings of the knife-edges.

1. If the various parts of the pendulum have masses m_1 m_2, etc., and are at distance s_1 s_2 from the point of suspension, and have moments of inertia about their centres of gravity equal to $m_1 k_1^2$, $m_2 k_2^2$ then the period of T_1 of the pendulum will be given by

$$T_1 = 2\pi \left(\frac{\Sigma m_1 (s_1^2 + k_1^2)}{g\Sigma m_1 s_1}\right)^{\frac{1}{2}}.$$

If all the mass had been concentrated at the centre of gravity at a distance l from the point of suspension the period would have been

$$T = 2\pi \left(\frac{l}{g}\right)^{\frac{1}{2}}.$$

Hence, the reduction to simple pendulum was given by multiplying the observed period by

$$\left(\frac{l\Sigma m_1 s_1}{\Sigma m_1 (s_1^2 + k_1^2)}\right)^{\frac{1}{2}}.$$

Most of the mass being concentrated near the centre of gravity, s_1 could be expressed as $s_1 = l - l_1$, where l_1 was a small distance which could be measured with a micrometer or reading microscope.

The correction involves a knowledge of l, but as the period is affected by this correction by less than one part in 1,000, it was not necessary to know l to an accuracy of more than a millimetre. To this degree of accuracy l could be determined either by direct measurement or could be calculated from a knowledge of the period of the pendulum and the approximate value of g.

For most of the parts of the pendulum s_1 (or l_1) and k_1 could be determined by direct measurement, but in the case of the knife-edge and mountings it had to be determined experimentally.

The period of the agate knife and mountings when swinging about the knife-edge was first measured. A thin straight rod was then inserted in the hole c (fig. 2), and the period again measured. From a knowledge of the two periods, the weights of the rod and the knife and mountings, and the dimensions

and position of the rod, both the s and k corresponding to the knife and its mountings could be calculated.

2. Let T_1, T_2, τ be the periods of the two pendulums and the period of coincidence for infinitely small amplitudes, T_1', T_2' and τ' the corresponding quantities for finite amplitudes.

Let $$T_2 > T_1 \quad \text{and} \quad T_2' > T_1'.$$

Then

$$\tau' - \tau = \frac{\tau\tau'}{T_2}\left(\frac{T_1'T_2}{T_1T_2'} - 1\right)$$

$$= \frac{\tau\tau'}{T_2}\frac{\bar{\alpha}_1^2 - \bar{\alpha}_2^2}{16},$$

where α_1^2, $\bar{\alpha}_2^2$ are the mean squares of the amplitudes of the two pendulums during the time τ'.

Assuming an exponential damping with which fair agreement was found

$$\bar{\alpha}_1^2 = \frac{A_1^2 - a_1^2}{\log_e A_1^2 - \log_e a_1^2},$$

where A_1 a_1 are the amplitudes of the pendulum at the beginning and at the end of the time τ'. A similar expression holds for $\bar{\alpha}_2^2$.

3. The correction for buoyancy has been made in the way adopted by Bessel. If T = period *in vacuo* and T′ = period in air

$$T^2 = T'^2 \frac{1 - \dfrac{m's'}{ms}}{1 + \dfrac{m'}{m}\phi},$$

where if δ_1, δ_2, δ_3, etc., represent the densities of the various parts of the pendulum, m_1, m_2, m_3, etc., their masses, s_1, s_2, s_3, etc., their distances from the axis of suspension, and Δ the density of the displaced air

$$m's' = \left(\Sigma \frac{m_1 s_1}{\delta_1}\right)\Delta, \qquad ms = \Sigma m_1 s_1,$$

$$m' = \left(\Sigma \frac{m_1}{\delta_1}\right)\Delta, \qquad m = \Sigma m_1.$$

ϕ is a constant depending only on the external form of the pendulum and not at all on the mass.

In practice the correction can be simplified by putting

$$T^2 = T'^2\left(1 - \frac{m's'}{ms}\beta\right)$$

where $\beta \doteq 1 + \phi$.

Bessel's method of determining β was to make observations with two pendulums of indentical outward form but of different densities, and to calculate the value of β from the two sets of readings. Bessel gave the value $\beta = 1 \cdot 75$. By swinging pendulums in air and *in vacuo* F. Baily* obtained a value of $\beta = 1 \cdot 86$. Using pendulums of the same form as those of Bessel and Baily the writer has by Bessel's method obtained the value $\beta = 1 \cdot 84$. The buoyancy correction has also to be considered for the standard pendulum.

4. If T be the period for undamped motion and T′ the period when the damping factor is k

$$T = T'\left(1 - \frac{l}{g}k^2\right)$$

where l and g have the usual significance.

If t be the time taken to reduce the amplitude by one half

$$k = \frac{\log_e 2}{t}.$$

For the smallest value of t obtained k was not greater than 1/1000, so that the effect of damping on the period was negligible.

5. In all these experiments the period of the pendulum with brass in the bob was taken as standard, other results being compared with that for brass. Suppose that with a certain brass cylinder inside the bob the micrometer reading was m inches, and with say ammonium fluoride it was l inches, the pendulum being longer in the second case. If L cms. be the length of the equivalent simple pendulum (this can be taken as the same in the two cases) the period in the case of ammonium fluoride must be multiplied by

$$\left(1 - \frac{2 \cdot 54\,(l - m)}{L}\right)^{\frac{1}{2}}.$$

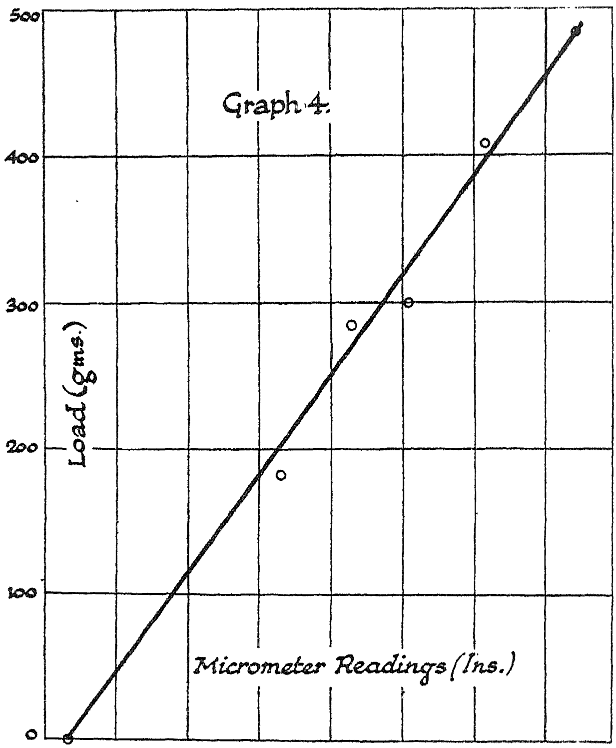
Again an accurate knowledge of L is unnecessary, assuming, of course, that $(l - m)$ is very small.

The chief causes of change in length are temperature and different loading of the wire, but two other causes might give rise to differences in the micrometer readings. The first is changes in length of the suspension wire due to accidental strain, but this does not appear to have caused much trouble, and a more important effect was that due to inaccuracies of the cylinder. Suppose that when one experiment was made the overall length of the cylinder was a cms., but that in a second experiment the length was b cms. Then the micrometer

* Baily, 'Phil. Trans.' (1832).

reading would be effected by an amount $= (a - b)$ cms. When, however, it is considered that observations were made with the cylinder one way up and then with it inverted, and that nearly all the mass was concentrated in the cylinder, it will be seen that the effective change in length of the pendulum (as shown by change of the period) would be only $\frac{1}{2}(a-b)$ cms.

In graph 4 some observations of the changes in length of the wire with



different loads are plotted. The ordinates represent load and the abscissæ micrometer readings in inches. The points lie approximately on a straight line, any deviations from the straight line being attributable, presumably, to changes in length of the cylinder. Corrections were made accordingly along the lines indicated above.

Another effect which alters the apparent length was found in the fact that the two faces of the embossed ends of the cylinder against which the adapters fitted were not perfectly parallel. This caused the rod which carried the steel ball to be inclined at a different angle to the vertical for the erect and inverted positions of the cylinder. The effect, however, was small, and obviously eliminates itself automatically in a comparative experiment.

6. The necessity for this correction was pointed out by Laplace, who showed that the bob and wire could not move as one piece, since the bob acquires and loses angular momentum about its centre of gravity, which could not be accounted for by forces which always passed through the centre of gravity. In reality, the bob turns through a slightly greater angle than the wire. The effect is easily calculable using Lagrange's equations.

Suppose a cylinder of height $2b$ to be suspended from a weightless thread of length a. Let the radius of gyration of the cylinder about its centre of gravity be K. Then by application of Lagrange's equations

$$\begin{vmatrix} a^2n^2 - ga & abn^2 \\ abn^2 & (b^2 + \mathrm{K}^2)\, n^2 - gb \end{vmatrix} = 0,$$

where $n = 2\pi/\mathrm{T}$, T being the period of the pendulum. This gives

$$\frac{g}{n^2} = \frac{a + \dfrac{b^2 + \mathrm{K}^2}{b}}{2}\left[1 \pm \sqrt{\left(1 - \frac{4ab\mathrm{K}^2}{(b^2 + \mathrm{K}^2 + ab)^2}\right)}\right].$$

The negative sign before the square-root represents a very rapid oscillation which would quickly die out. It can easily be observed when the pendulum is first started, but observations were never made until the pendulum had been swinging for some 20 minutes, and by that time the rapid oscillation had always died out. The effect was less if the pendulum was started by hand than if mechanical methods were used, and consequently the former method was preferred.

Neglecting this negative sign, the expression for g/n^2 becomes

$$\frac{g}{n^2} = a + b + \frac{\mathrm{K}^2}{a + b} + \frac{a\mathrm{K}^4}{b\,(a + b)^3} - \frac{a\mathrm{K}^6}{b^2\,(a + b)^4} - \dots .$$

The last term is negligible and the whole expression is the same as that obtained by Bessel by another method.

For the rigid pendulum

$$\frac{g}{n^2} = a + b + \frac{\mathrm{K}^2}{a + b}.$$

Thus, to correct for non-rigidity of this connection, the observed period should be multiplied by $1 - \dfrac{a\mathrm{K}^4}{2b\,(a + b)^4}$, K being small compared to $(a+b)$.

The correction for non-rigidity of connection between the suspension-wire and the knife mountings can be calculated in a similar manner, but appeared to be quite negligible in these experiments.

Results.

The first actual measurements were for the determination of the damping factor β; having determined this it was possible to proceed with the comparison of gravitational accelerations of various bodies.

The substances under test were, in the case of metals and mahogany, turned into cylinders which fitted accurately into the hollow cylindrical bob. The body was clamped in position by a side screw shown in figs. 3 and 4. In the case of ammonium fluoride and paraffin wax, special methods of filling are discussed below.

Lead and Steel.

Experiments with lead and steel were carried out with the Cambridge and Paul Cylinder. The lead pendulum was found to have a period of 25 parts in 10,000,000 greater than a pendulum containing brass which was used for comparison. This represents a difference of five parts in a million in the gravitational accelerations, and as only 4/7 of the entire weight was lead (the remainder was composed chiefly of the brass bob), the experiment shows that the gravitational acceleration of brass is not greater than that of lead by more than one part in 120,000. This represents a difference which is certainly not greater than the experimental error.

The experiments with steel gave a gravitational acceleration for steel less than that for brass of one part in 50,000. This is the least satisfactory of any of the results obtained and is probably due to the magnetic properties of steel.

The experiments on lead and steel (both substances had been tested by Bessel) served merely as a test of the accuracy of which the method was capable. They were followed by some experiments on ammonium fluoride and paraffin wax, but the experiments with these substances were of comparatively little value owing to the fact that the weights of fluoride and wax which could be put inside the Cambridge and Paul Brass Cylinder were small in comparison with the weight of the container.

Ammonium Fluoride.

The first series of experiments with the Hilger Brass Cylinder was the comparison of the gravitational accelerations of brass and ammonium fluoride. In order to prevent corrosion by the fluoride the cylinder was gilded inside and out.

The experiments with fluoride were troublesome on account of the difficulty

of filling the cylinder and keeping it full. The filling was done very slowly, each little bit being well pounded in; when the cylinder was full the end was carefully slid on and screwed down. It is not necessary that the cylinder be absolutely full as long as the substance inside does not move about. Here, however, the difficulty arose. After having been pounded in, the fluoride seemed to cement itself together (continual weighing, however, showed that this was not accompanied by loss of weight), and to shrink considerably, becoming quite loose inside the cylinder. The only way in which it was found possible to fill the cylinder was first to well pound in some fluoride until the cylinder was full, then to close the cylinder and let it stand for a couple of days. The cylinder was then opened, the fluoride re-pounded and more fluoride added to make up for the shrinkage. This process was continued several times until finally a hard mass of fluoride which remained stationary in the cylinder was obtained. The constancy of the period of the pendulum was itself a very delicate test of the adhesion of the fluoride.

The gravitational acceleration of ammonium fluoride was found to be five parts in 1,000,000 greater than that of brass—a variation well within the limits of experimental error.

Bismuth.

After the experiments on ammonium fluoride it was necessary to take the whole pendulum to pieces in order to give it a thorough clean up. As it was impossible to put the adapters on to the wires in exactly the same position as before, it was necessary to make a further determination of the period of the pendulum with brass in the cylinder.

This was followed by some experiments on bismuth. C. F. Brush* has claimed to have established by several methods a difference in the gravitational constants of zinc and bismuth. This he suggests is due to the diamagnetic properties of bismuth, and claims that his results gave support to a kinetic theory of gravitation which he had developed.†

A sample of bismuth which had been moulded and carefully lathe-turned into a cylinder was tried in the pendulum. The difference in the measured gravitational accelerations of brass and bismuth lay well within experimental error.‡

* Brush, 'Phys. Rev.,' p. 125 (Aug. 1921).

† *Cf.* Brush, 'Nature,' vol. 86 (1911).

‡ *Cf.* Potter, 'Phys. Rev.' (Feb. 1922).

Paraffin Wax.

The next substance tested was paraffin wax. The filling of the pendulum bob with paraffin wax was a process requiring considerable care. After removing one end of the hollow cylinder a little liquid wax was poured in, and this was made to solidify from the bottom by keeping the top surface warm by the help of a tiny flame. In this way the cylinder was filled by adding small quantities of wax and allowing each bit to solidify before adding more. When the cylinder was quite full and the wax solid, but still warm, the top of the wax was made to come flush with the top of the cylinder by cutting it with a very sharp knife. Subsequent cooling made the wax contract and sink about 0·25 mm. below the top of the cylinder, so that the top could be put on without interference from the wax. The acceleration of paraffin wax was equal to that of brass to within the limits of experimental error.

Aluminium.

The next and last experiment of this series was carried out with duralumin (95 per cent. aluminium). Again the results were the same as those for brass.

Since these experiments were completed more details of Brush's experiments have been published.* In this paper he claims to have found great differences between the constants of gravitational attraction for various substances. These experiments were carried out with a modification of the Boy's Balance, and some of the experiments were supported by pendulum observations made by Brush. Brush does not appear to have compared bismuth and aluminium directly by means of the pendulum, but with the gravity balance he claims to have shown that the constant of gravitational attraction is about 100 per cent. more for aluminium than for bismuth. Accepting Brush's kinetic theory of gravitation it is not necessary to assume that because the gravitational constants of these bodies were vastly different, their accelerations in the earth's gravitational field would be very different, but the differences which Brush obtained in pendulum experiments should have been easily detected in the present experiments.

It is interesting in view of this to see that in the experiments carried out by the writer no difference could be detected between the gravitational accelerations of aluminium and bismuth, the two substances between which Brush found the greatest divergence in the values of the respective constants of gravitational attraction. Brush appears to have ignored the buoyancy correction in his

* 'Proc. Ann. Phil. Soc.,' vol. LX, No. 2 (1921).

pendulum experiments. Using 1·84 as the buoyancy factor, the correction which he should have applied comes out of the right order to explain his anomalous results.

Paraffin Wax and Mahogany.

After these results using the Hilger brass cylinder were obtained, some further experiments were carried out with paraffin wax in the Hilger duralumin cylinder. These experiments were somewhat more difficult, and perhaps less reliable on account of the rapid damping of so light a cylinder. The experiments, however, showed no difference greater than that attributable to experimental error in the gravitational accelerations of wax and brass.

One series of experiments was also made with mahogany (which also contains hydrogen), but again the same result as with brass was obtained.

A summary of the results is given below.

Substance.	Corrected Period of Pendulum τ = period of standard.	Weight of substance (gms.).	Weight of whole pendulum.	Calculated value of acceleration.
1st Group—				
Brass	$1 \cdot 0004172\tau$	pendulum	all brass.	g
Lead	$1 \cdot 0004193\tau$	408	712	$0 \cdot 999992g$
Steel	$1 \cdot 0004220\tau$	284	592	$0 \cdot 999980g$
2nd Group—				
Brass	$0 \cdot 9999185\tau$	pendulum	all brass.	g
Ammonium fluoride	$0 \cdot 9999175\tau$	85	233	$1 \cdot 000005g$
3rd Group—				
Brass	$0 \cdot 9999885\tau$	pendulum	all brass.	g
Bismuth	$0 \cdot 9999895\tau$	79	228	$0 \cdot 999994g$
Paraffin wax	$0 \cdot 9999865\tau$	70	219	$1 \cdot 000012g$
Duralumin	$0 \cdot 9999905\tau$	147	296	$0 \cdot 999992g$
4th Group—				
Brass	$1 \cdot 0000520\tau$	75	172	g
Paraffin wax	$1 \cdot 0000490\tau$	68	164	$1 \cdot 000014g$
Mahogany	$1 \cdot 0000485\tau$	73	169	$1 \cdot 000015g$
5th Group—				
Brass	$0 \cdot 9999365\tau$	75	172	g
Paraffin wax	$0 \cdot 9999335\tau$	68	164	$1 \cdot 000014g$

A summary of the values of the gravitational accelerations of the various substances is given below. The acceleration of brass is taken as g.

Lead	$0 \cdot 999992g$
Steel	$0 \cdot 999980g$
Am. fluoride	$1 \cdot 000005g$
Bismuth	$0 \cdot 999994g$
Paraffin wax	$1 \cdot 000013g$
Mahogany	$1 \cdot 000015g$
Duralumin	$0 \cdot 999992g$

Eötvos Balance.

It is somewhat striking that the three substances, Ammonium Fluoride, Paraffin Wax and Mahogany, which are "rich in hydrogen" appear to have a slightly greater gravitational acceleration than do the other substances. Everything however depends finally on the measurement of a period, and, if we neglect the case of steel, the greatest deviation in the period of any pendulum from the period of the corresponding brass pendulum was only one part in 300,000, a deviation which is not bigger than possible experimental error.

An attempt, however, was made to increase the accuracy of these tests by using an Eötvos balance. A small model similar to that used by Zeeman* was constructed and mounted on a stone pillar in the basement of King's College. It was found impossible, however, with this apparatus to get an accuracy greater than that obtainable with the pendulum. This was due largely to the vibrations which are always present in a great city like London.

Later, negotiations were opened with Messrs. Ferdinand Süss & Co., of Buda-Pest, with a view to the purchase of an Eötvos balance (made by them under the supervision of Dr. Pekar—a collaborator of von Eötvos), but the price of the instrument was prohibitive.

Summary.

The gravitational accelerations of lead, steel, ammonium fluoride, bismuth, paraffin wax, duralumin and mahogany have been compared with that of brass, and no difference greater than that attributable to experimental error has been found. An accuracy of at least one part in 50,000 has been obtained. Special attention has been given to two substances, ammonium fluoride and paraffin wax, which have large hydrogen contents.

In conclusion I wish to express my gratitude to Prof. O. W. Richardson for initiating this research and for supervising the experiments.

* Zeeman, 'Verh. d. K. Ak. van Wet.,' vol. 26, p. 451 (1917).

The Thermionic and Photo-Electric Properties of the Electro-Positive Metals.

By A. F. A. Young, B.Sc., King's College, London.

(Communicated by Prof. O. W. Richardson, F.R.S. Received July 4, 1923.)

Introduction.

The magnitude of the purely thermal emission of electrons from the alkali metals has not been fully determined. The first investigation was by Prof. O. W. Richardson* on the emission from sodium. This was contained in a horizontal steel tube in which a wire stretched parallel to the axis served as collecting electrode. The conditions, however, were such that there was a considerable evolution of gas in the apparatus during the heating, and the currents obtained showed no approach to saturation. The negative currents at constant potential difference agreed with the emission formula

$$i = A_1 \varepsilon T^{\frac{1}{2}} e^{-b/T}$$

in which $A_1 = 10^{31}$ $\qquad b = 3 \cdot 16 \times 10^4$.

K. Fredenhagen† also investigated the emission from sodium and potassium. He worked with a glass apparatus and purified the metal by a two or threefold distillation. In his final experiments the tube was evacuated as far as possible and then sealed off. Observations were then taken while the alkali metal was heated continuously for many hours. The currents obtained were found to depend largely on the treatment of the tube, and showed a tendency to decrease with the duration of the experiments. Fredenhagen thus concluded that the observed currents were not due to the metal itself, but to some gas which could be partly removed by repeated distillation of the metal, and by long heating in an apparatus in which the metal was continually vaporising, condensing, and flowing back to its original position. He also concluded that the gas was probably hydrogen, although he had no direct proof. The currents were usually greatly reduced by the action of an induction coil discharge, and he found that a connection existed between the magnitudes of the thermal currents and the photo-electric currents in so far as they were found to decrease together.

* 'Phil. Trans. Roy. Soc.,' A, vol. 201, p. 532 (1903).

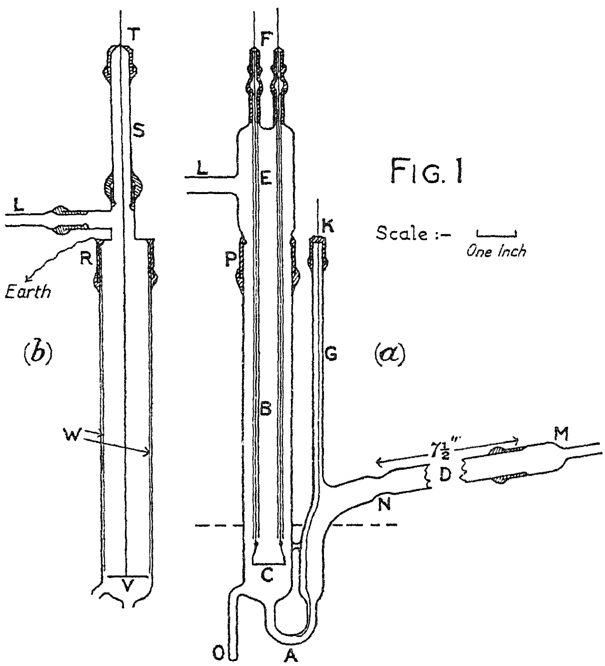
† 'Phys. Zeits.,' vol. 12, p. 398 (1911); 'Verh. d. Deutsch Phys. Ges.,' vol. 14, p. 384 (1912); *ibid.*, vol. 16, p. 201 (1914).

In the present work a fresh attempt is made to determine the magnitude of the thermionic emission from the alkali metals. Observations have at the same time been made on the photo-electric emission with regard to the threshold frequency.

Experimental Arrangements.

An attempt was first made to heat the alkali metal in a form of glass apparatus, but in each case this came to grief through contact with the hot metal before any readings could be taken.

Measurements were then made with an apparatus constructed of transparent quartz, the form of which is shown in fig. 1 (*a*). It consists essentially of the



U-tube A which holds the alkali metal, the larger tube B containing the collecting electrode C, and the sloping tube D, into which short sticks or lumps of the metal could be placed. E is a glass cap which is sealing-waxed on to the end of the quartz tube at P. The collecting electrode C consisted, at this stage, of a piece of platinum foil usually about 19 mm. long × 9 mm. broad × 0·005 mm. thick, welded to short thick platinum leads, which in turn were welded to fairly thick copper leads passing through the brass caps F and contained in two thin glass tubes which were sealing-waxed into the two

glass tubes protruding from the cap. By this arrangement the platinum electrode could be made red-hot by passing a current of from 4 to 6 amps. through it. The tube G, closed by a brass cap K, contained a platinum-copper lead which made contact with the alkali metal in the U-shaped tube A.

In the later experiments, in which the currents at lower temperatures were measured by means of a Wilson tilted electroscope, the glass cap E with the electrode C (fig. 1 (*a*)) were replaced by the arrangement shown in fig. 1 (*b*). R is a copper cap fitting closely on the quartz tube and attached by sealing wax. Into this was sealing-waxed the short quartz tube S, supporting the brass cap T, through which passed a copper wire ending in a thin circular perforated copper plate V, of about 19 mm. diameter, which acted as electrode. The glass tube L to the pumps was attached by sealing-wax to the copper cap. A thin copper cylinder W, perforated with about 1 cm. diameter holes, was also fitted inside the main quartz tube and reached down to within about 1 cm. of the electrode V. This cylinder, and the copper cap R, remained connected to earth during the measurements, disturbances caused by the charging up of the metal condensed on the walls of the tube thus being prevented. The short tube S served to insulate the central electrode; it could be kept clear of any condensed metal by a slight heating at its centre with a small flame.

The evacuation was effected by means of a rapidly working mercury-vapour condensation pump in conjunction with a rotary Gaede pump backed by a "Geryk" oil pump. The pressures were measured on a McLeod gauge, which could be connected to the high-pressure side of the condensation pump or through a liquid-air trap to the quartz tube itself.

The method of setting up the tube was as follows. The glass cap E with the platinum electrode, or the copper cap R with quartz tube, copper electrode and cylinder, were attached by sealing-wax to the quartz, and the tube fixed in position by attaching the tube L from the condensation pump to the cap.

The alkali metal was then rolled or cut into short sticks from ½ to 1 inch in length and freed from naphtha by being placed in a tube exhausted by an oil pump. They were next placed so as to be just separated in the sloping tube D of the apparatus. The glass tube M was at once attached to the quartz with sealing wax and fused to a tube which connected to a point in the evacuating system between the Gaede and condensation pumps. The apparatus was then exhausted. When it was certain that there were no leaks the U-tube was filled with alkali metal by gently warming the foremost piece until the bright metal ran free from the outer crust and, aided by judicious

tapping, fell over into the U-tube. The crust was held back by the constriction N. There was always a considerable evolution of gas during the process, especially in the case of potassium, the pressure perhaps rising to a few centimetres of mercury. As soon as the U-tube was partly filled, the condensation pump was set working. More metal could be brought down when required by melting another piece; any excess of the metal was prevented from swamping the electrode by the side tube O. By this method the space over the emitting surface could be exhausted to a high degree by the condensation pump, while the refuse from the metal was only exhausted by the Gaede pump. This method of obtaining a clean surface was chosen in preference to the process of continued distillation, since it is doubtful whether such a process really results in an absolutely uncontaminated surface. With the method used, a thin film of oxide at first formed on the surface of the metal, but, apparently after a further heating, during which the film was broken up and most of the remaining gas driven out of the metal, the surface would remain bright in the vacuum indefinitely.

The alkali metal was heated by surrounding the lower part of the tube up to the neighbourhood of the broken line in fig. 1 (*a*) by an electric heater. Two of these were used. One consisted of a non-inductive double spiral of Eureka wire wound on mica on the outside of a copper calorimeter. The coil and calorimeter were enclosed on the outside by asbestos, and when in position the top of the heater was closed in by uralite cut to the shape of the quartz tube and packed round by moist asbestos. A circular aperture, 1·6 cm. in diameter, was cut in the side of the asbestos and through the asbestos packing so as to expose the windings of the heater and a layer of transparent mica. This served as a window through which the alkali metal could be illuminated whilst it was maintained at a temperature above that of the room. The mica prevented air convection through the aperture. A similar second heater, only without the aperture, was constructed of welded iron, so that the tube could be heated by a mercury bath. The temperatures were measured by a mercury in glass thermometer, reading to 370° C., which was passed through an aperture in the uralite so that its bulb rested on the lowest part of the U bend.

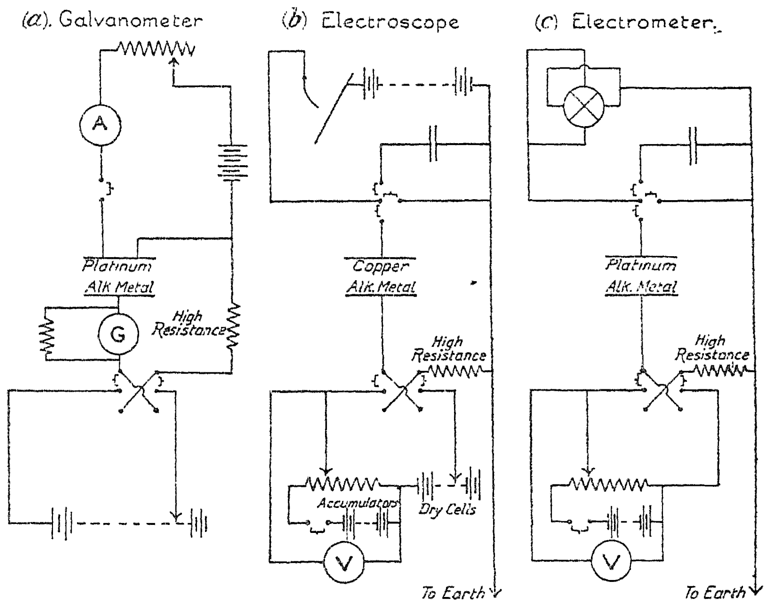
Two arrangements were used for measuring the thermionic current (1) using a galvanometer, (2) using a Wilson tilted electroscope. The galvanometer was connected to the electrodes of the tube in series with a battery of small dry cells, the number of which could be varied, and a high resistance of about 10^6 ohms. This served to prevent damage from short-circuits in the tube, and since currents of less than 10^{-7} ampere were measured, it did not reduce

appreciably the potential difference between the electrodes. The sensitivity of the galvanometer was $2 \cdot 5 \times 10^{-9}$ ampere per centimetre deflection per metre scale distance; it could be reduced by shunts if necessary. An auxiliary circuit containing a key, resistance, ammeter, and accumulators, was sometimes connected to the platinum electrode so as to be able to heat it. The tilted electroscope used with the arrangement in fig. 1 (*b*) was connected by shielded wires to the central electrode, the alkali metal being connected through the battery and high resistance to earth. The heating vessel, being insulated from the windings, was also earthed. The motions of the electroscope leaf were observed by means of a reading microscope with a scale in the eyepiece. The sensitivity was usually about 70 divisions per volt. By the use of an additional capacity, variable in steps from $0 \cdot 001$ to $0 \cdot 3$ microfarad, currents from 10^{-14} to 10^{-8} ampere could be measured in succession. Small potential differences were applied to the electrode by replacing the dry cells by accumulators and a potentiometer. Fig. 2 gives details of the various electrical connections.

The photo-electric currents were measured either by means of the tilted

FIG. 2

DIAGRAM OF CIRCUITS



electroscope, with the connections as described, or, when the galvanometer was used to measure the thermionic currents, with an electrometer in place

of the electroscope. Monochromatic light was obtained by means of a Hilger quartz monochromatic illuminator and a 100 candle-power Pointolite lamp. The illuminator was one provided with accessories for use also as an infra-red spectrometer. The light from the lamp was concentrated on the slit of the illuminator by means of a $3\frac{1}{2}$-inch glass condensing lens. The quartz tube was screened from the light of the room by enclosing it in a large cardboard box blackened on the inside. The tube could be viewed by removing part of the front of this, through which the telescope of the illuminator was also made to pass. The light from the illuminator usually fell on the surface of the metal in the tube at an angle of incidence of about 70 degrees.

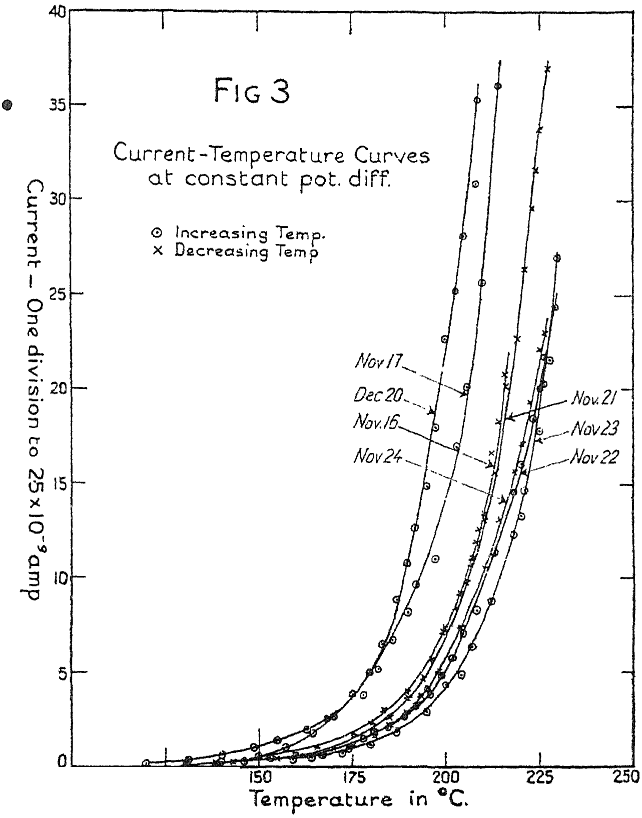
Behaviour of Sodium.

Sodium was first used with the apparatus as in fig. 1 (*a*), the currents being measured by the galvanometer, but in each case no measurable current could be obtained with the sodium as positive or negative electrode for temperatures up to 390° C., even with potential differences of 300 volts. The heating was accompanied by an evolution of gas, the backing pressure of the condensation pump in some cases rising to 0·01 mm. of mercury. An inspection of the sodium showed that the surface was quite bright during the heating, but at the higher temperatures it was disturbed by the formation of bubbles of gas which could not readily escape owing to the large surface tension of the metal. The presence of an electric lamp near the tube caused a measurable photo-electric current on the galvanometer. At a temperature of 390° C. the quartz tube began to show a brown discolouration, due to reaction with the sodium. As, therefore, at higher temperatures the results would have been complicated by obvious chemical reaction, attention was turned to potassium, with which measurable currents were obtained.

Behaviour of Potassium.

Measurements at Higher Temperatures using the Galvanometer.—After the temperature had been raised to 250–300° C. for the first time following the charging of the tube with potassium, the tube being arranged as in fig. 1 (*a*), fairly consistent constant voltage current-temperature curves could always be obtained when the potassium surface was the negative electrode. Fig. 3 shows a series of such curves obtained with the same potassium at intervals lasting over one month, these constituting the first observations on potassium. The potential difference for all the curves was 370 volts. The tube was exhausted by the mercury vapour pump before and whilst taking a set of readings, and

the vacuum allowed to become poor between each set. At this stage only the backing pressure to the mercury-vapour pump could be observed. This



was found to increase in all the sets of readings except that for November 16 from about 10^{-4} mm. to about 7×10^{-4} mm. of mercury during the heating; in the other case the range was $2 \cdot 8 \times 10^{-3}$ to 10^{-3} mm. of mercury. The points marked ⊙ were obtained whilst the temperature slowly rose, those marked × whilst it slowly fell, a single curve being obtained in about $1\frac{1}{2}$ hours. After the potassium had been first heated, a certain amount of it was deposited on the walls of the quartz tube, and to a slight extent inside the glass cap, the part of the tube inside the heater remaining free however, thus preventing a short-circuit. Drops of the metal also accumulated on the platinum electrode, since for these readings it was not heated electrically. The current with the platinum as negative electrode was, however, at the most less than 0·01 of the current when the potential was reversed.

In some of the later observations with the galvanometer it was found

necessary to raise the temperature to about 230° C. before any appreciable emission could be obtained, at which temperature the emission would suddenly increase and then remain steady. As the temperature was rising the currents were small and irregular, as can be seen from the two sets of readings in Table I and fig. 4. The successive readings of the pressure given below were obtained by connecting the McLeod gauge to the tube itself.

Table I.

(a)			(b)		
Temp. (° C.)	Galvanometer deflection (cm.)	Pressure (mm. mercury).	Temp. (° C.)	Galvanometer deflection (cm.)	Pressure (mm. mercury).
136	0·2	$<10^{-6}$	128	2·4	$<10^{-6}$
165	2·0	—	149	3·7	—
190	1·5	10^{-6}	164	3·6	$<10^{-6}$
205	1·6	10^{-6}	205	5·6	—
220	2·1	—	220	12·2	—
238	6·9	10^{-5}	224	17·6	2×10^{-5}
240	Large	10^{-6}	235	Large	10^{-5}
218	,,	$<10^{-6}$	208	38·8	—
182	35·6	—	202	26·6	$<10^{-6}$
168	12·2	$<10^{-6}$	180	6·4	—
120	0·6	$<10^{-6}$	147	0·8	$<10^{-6}$

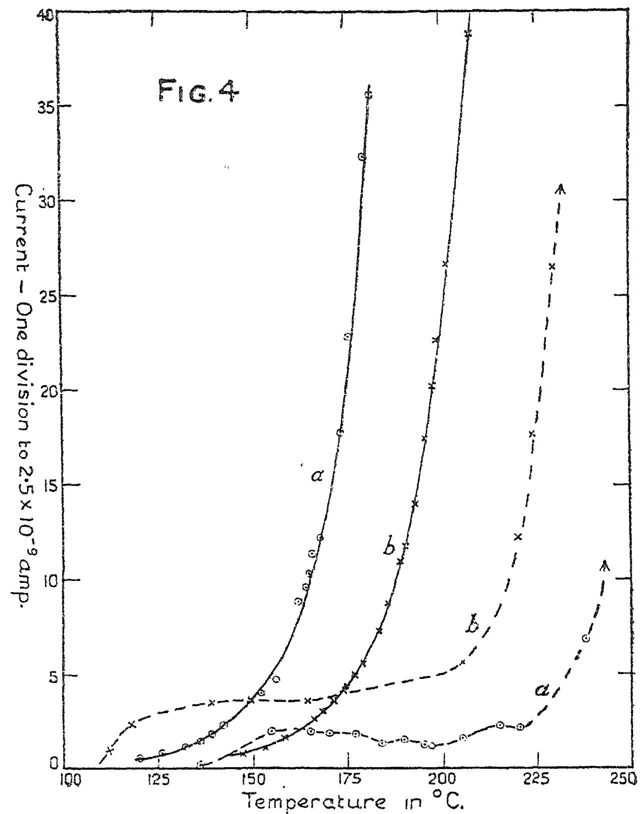
They show how the pressure varies even if the actual values are somewhat inaccurate; where $<10^{-6}$ is indicated the gas column in the capillary of the gauge could be compressed until extremely minute without effecting a difference in the levels of the mercury surfaces.

It was found that the glowing of the platinum electrode when not taking a reading, so that no metal condensed on it, did not affect the currents in any definite way, so that this was afterwards neglected.

Measurements at Lower Temperatures, using the Electroscope.—By means of the electroscope, the currents from the potassium could be measured in some cases at almost room temperature. The experimental arrangements were those already described with reference to the electroscope and to fig. 1 (*b*). It will be most convenient to deal first with the temperature variation at constant potential difference, which was 235 volts unless otherwise stated, and then to consider the relation between current and potential difference at constant temperature.

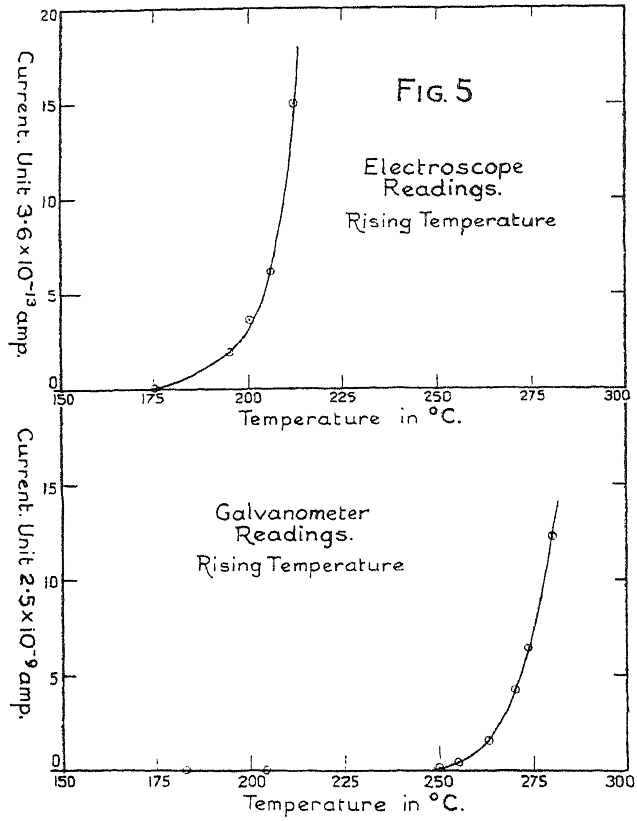
The first time that the tube was set up as indicated in fig. 1 (*b*) it was found

that at first no measurable currents were obtained with the electroscope until the temperature had reached 100° C. or 150° C., and the current at 200° C.



was of a much smaller order than that at 200° C. in the case of the above galvanometer measurements with the apparatus as in fig. 1 (*a*). Fig. 5 shows some actual observations. The raising of the temperature to between 250° and 300° C. also did not bring about a large increase in the current at a given temperature in the manner in which it did before. An examination of the potassium showed that the surface was quite bright and appeared like clean mercury. After the potassium had been heated several times at intervals, however, it was found that the currents had become measurable at a quite low temperature, just above that of the room. On further raising the temperature a peculiar effect was observed. The current would continue to increase with increasing temperature, until a temperature was reached at which it suddenly began to fall off as the temperature was further increased, until it reached a very low value. Some signs were then found of a recommencing

increase with temperature. On allowing the temperature to fall, the current would suddenly increase again to a high value, and then fall in a regular

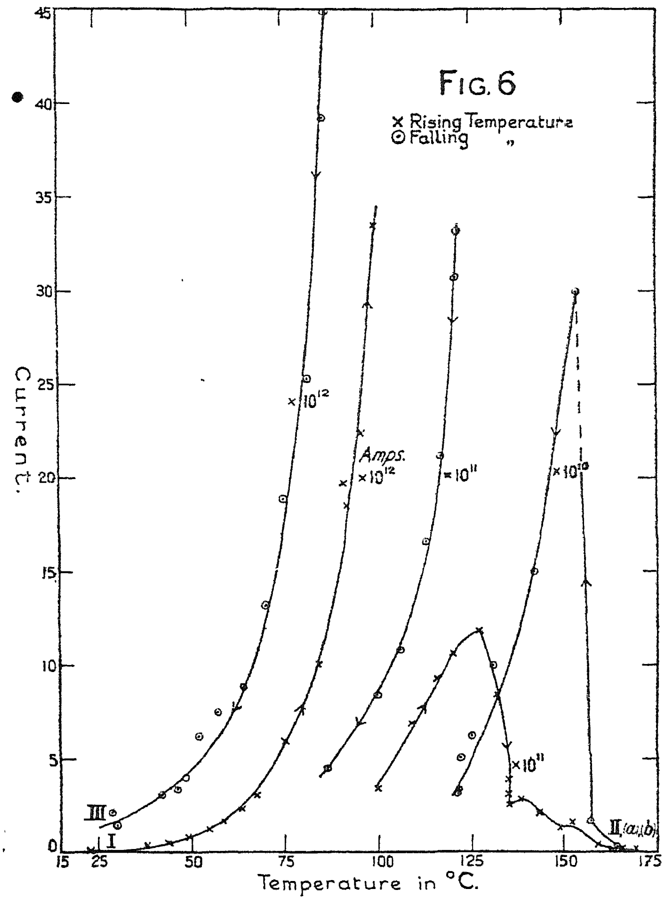


manner as the temperature fell, the value of the current at a particular temperature being larger, however, than the corresponding value with rising temperature. A typical case is shown in fig. 6. The ordinates show the current in amperes multiplied by the factor indicated, and the arrowheads on the curves show the order of taking the readings. The sudden decrease of the current at first set in at a temperature of approximately 125° C., but after several heatings of the tube the critical temperature became higher. The following were the succession of values observed :—

125°, 140°, 127°, 140° C.

After this, the tube was heated on five successive occasions to about 225° C. without there being any signs of falling-off of the currents with increasing temperature. On the sixth occasion a slight decrease set in at 160° C. Then

followed ten heatings of the tube to 215° C. without any signs of decrease in current with rising temperature except for the fourth heating, in which a



decrease set in at 160° C. By the time of the last heating the potassium had been in the tube for eleven weeks. In the case of the later heatings a certain amount of oxide or solid matter could be seen on the surface of the potassium, but the centre part of the surface remained bright, being continually renewed at the high temperatures, as in Fredenhagen's experiments, by the fall of drops from the walls of the tube. In all the above cases the pumps were kept continually running during the measurements, but it was found that a slight rise in pressure at higher temperatures could not be prevented. This rise, however, was generally smaller after the potassium had been heated in the tube several times. There are two explanations possible to the observed effects, (1) that the falling-off of the current is due to generation of gas in the apparatus

which contaminates the surface of the potassium, (2) that the large currents measured were due to some structural modification of the surface of the pure potassium, which formed after continued heating. These possibilities will be considered again later.

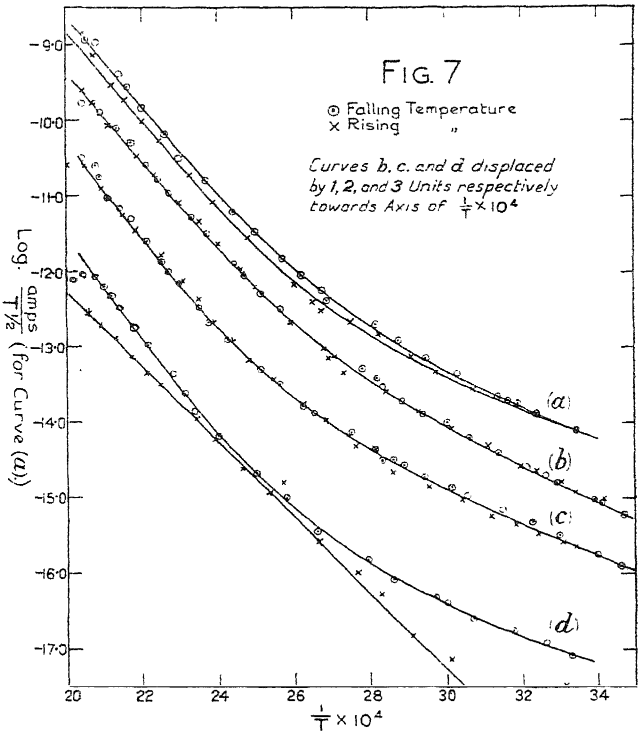
The variation of current with temperature, apart from the above-mentioned phenomenon, can be most readily seen by assuming the currents at a particular potential difference to obey the emission formula $i = a\,\varepsilon\,A_1\,T^{\frac{1}{2}}\,e^{-b/T}$, ... (i)

where i = total current from the surface in amperes,
a = area of surface in square centimetres,
ε = electronic charge in Coulomb.
T = absolute temperature,
A_1 and b are constants,

and plotting $y = \log_{10} i - \frac{1}{2}\log_{10} T$
against $x = 1/T$
which gives $y = -b\log_{10} e \,.\, x + \log_{10} a\,\varepsilon\,A_1$ .... (ii)

This has been done for some of the cases in which the falling-off did not occur, in fig. 7. To be sure that the effect was not varying considerably with time, it was necessary to go over a curve twice, while the vacuum was maintained by continual pumping. Thus with regard to fig. 7, curves (a), the temperature of the potassium was raised to 220° C. and slowly allowed to fall to nearly room temperature, and then slowly raised to the initial temperature. The points ⊙ were obtained with falling temperature and the points × with rising temperature, the time necessary to complete the series being $4\frac{1}{2}$ hours. It will be seen that the currents were very steady, although the value for rising temperature fell slightly below that for falling temperature (at higher temperatures about two-thirds of the value). The curves (b) show a case in which no appreciable variation in the current at a particular temperature occurred, although the total time was $4\frac{3}{4}$ hours. For the curves (c) the complete time was $5\frac{1}{2}$ hours. It will be noticed that the linear relation to be expected if A_1 is independent of the temperature and b independent of, or a linear function of, the temperature in equation (ii) apparently does not hold. If $\log_{10} i - 2\log_{10} T$ is plotted against $1/T$ the deviation from rectilinearity is equally marked. This, however, may be partly due to some complication arising from the presence of potassium vapour in the tube, which will be considered with regard to the current potential difference relation. A linear relation was sometimes obtained on first heating the potassium after it had been left unheated for a day or more. Such an instance in which the tube

had been left untouched for four clear days is shown under (*d*) in fig. 7. The non-linear relation was obtained again as shown on allowing the potassium



to cool. Not much significance, however, can be attached to this, since the surface was probably tarnished in the beginning, and the potassium absorbed a considerable amount of gas.

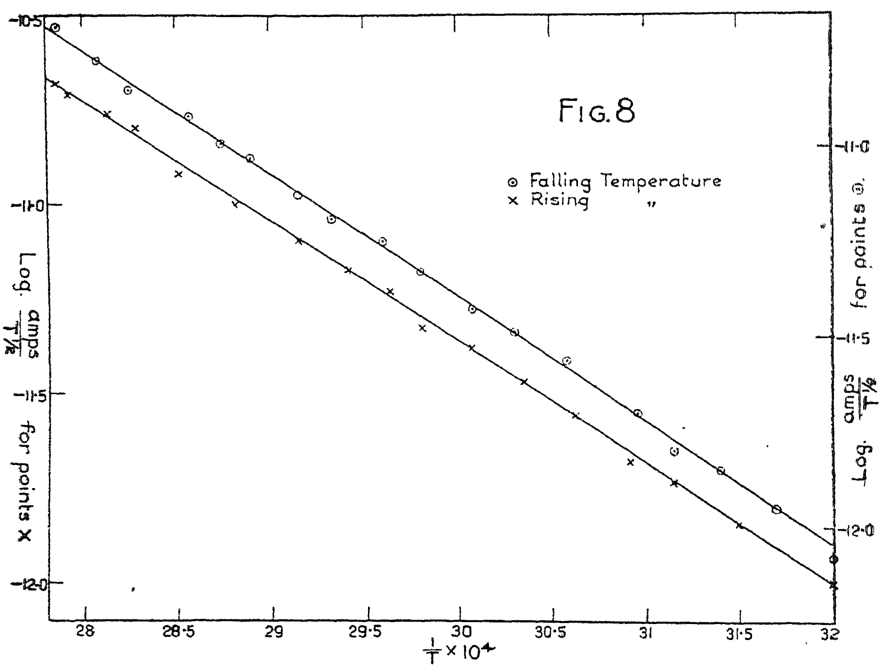
The currents in the neighbourhood of 200° C. in these experiments with the electroscope, provided that the falling off did not occur, were of the same order as those previously obtained with the apparatus as it was first set up, using the galvanometer. No definite decrease with duration of the experiment was observed; such variations as did occur could be accounted for by alterations in the emitting area caused by the accumulation of particles of oxide or solid substance. Below in Table II are the values of $y = \log_{10} i - \frac{1}{2} \log_{10} \mathrm{T}$ for the temperatures 180° C. and 30° C., together with the measured diameter of the surface, for the curves which did not exhibit the reduction effect the observations all being made with the same potassium.

Table II.

Date.	Value of $y = \log_{10} i - \frac{1}{2}\log_{10} T$.		Estimated diameter of surface.
	Temp. 180° C.	Temp. 30° C.	
October 17	− 9·8	−13·1	1·8 cm.
18	−10·2	−14·1	1·8 ,,
23	−10·0	−14·0	1·8 ,,
25	−10·4	−14·6	1·8 ,,
31	− 9·1	−13·0	2·0 ,,
November 3	− 9·2	−13·0	2·0 ,,
9	− 8·8	−12·7	2·0 ,,
13	− 8·8	−13·0	2·0 ,,
15	− 9·6	−12·5	2·0 ,,
27	− 9·6	−13·8	2·0 ,,
29	−10·0	−14·0	2·0 ,,
December 1	− 9·5	−13·2	2·0 ,,

The Change of State Solid–liquid of the Potassium.

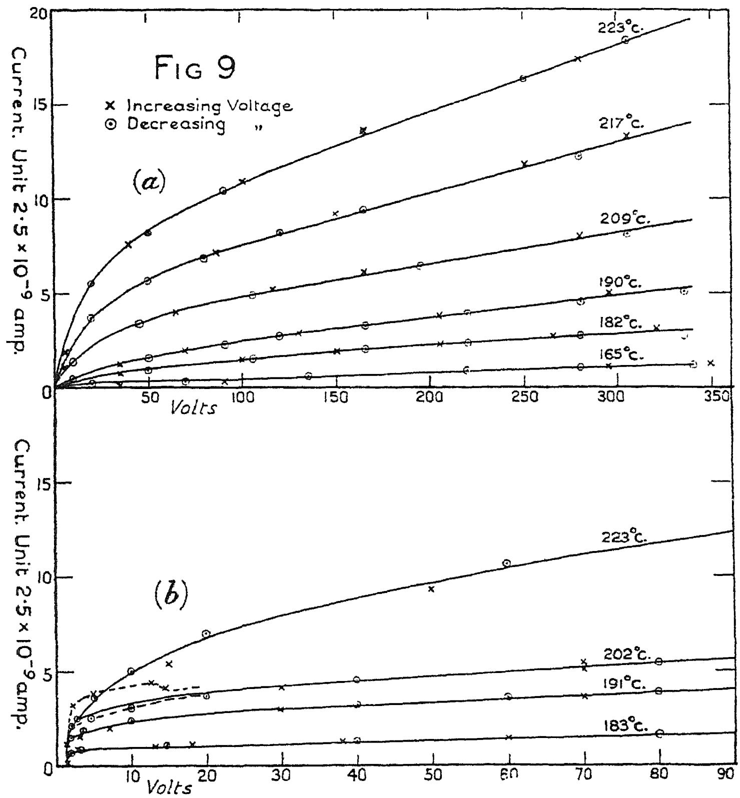
An important point with regard to the curves in fig. 7 is that the currents are continuous in the neighbourhood of the melting point of potassium, 62·5° C., which corresponds to the abscissa $1/T \times 10^4 = 29·8$. All points to the left of this correspond to liquid, and those to the right to solid potassium. A room temperature of 15° C. corresponds to $1/T \times 10^4 = 34·7$. Special attention was paid to the behaviour of the currents in the neighbourhood of the melting



point, and fig. 8 shows two curves drawn from a number of readings taken at temperatures between 40° C. and 85° C. An inspection of the tube showed that the metal was certainly solid at the former temperature and liquid at the latter; moreover, the heater containing mercury was used for these readings, so that the temperatures should be accurately estimated. The curves show that there is no abrupt change in the rate of increase of the currents with temperature or in their absolute values during the change from solid to liquid state or *vice versa*.

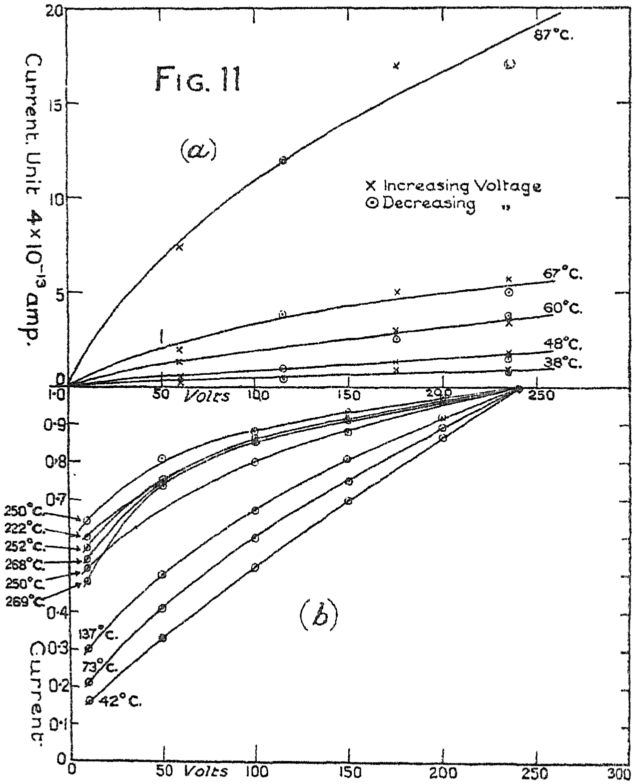
The Relation between Current and Potential Difference at Constant Temperatures.

The relation between current and applied potential difference appears somewhat complicated. Figs. 9 (*a*) and (*b*) show the type of curves obtained



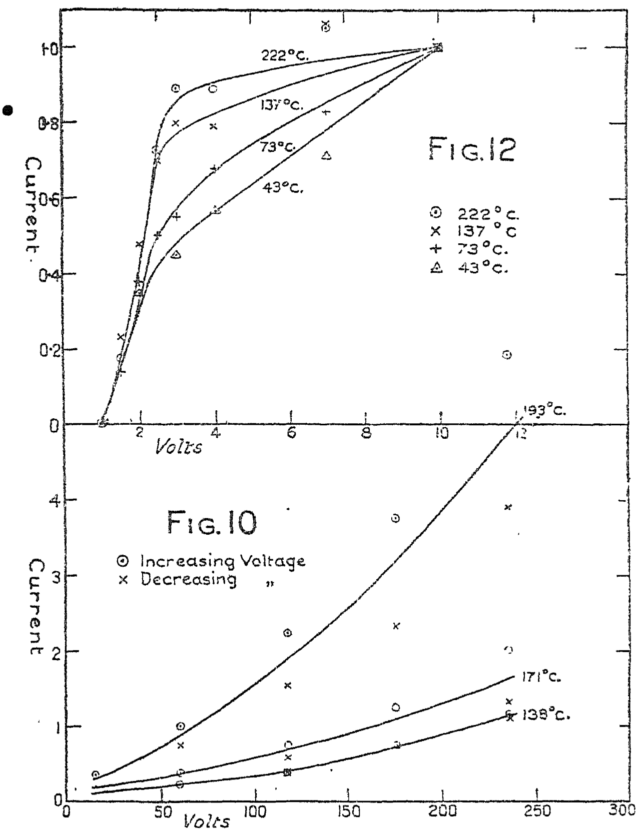
with the potassium as negative electrode when the arrangement in fig. 1 (*a*) was used in conjunction with the galvanometer. The currents when the potential was reversed were in every case, including those cited below, entirely

negligible compared with the former. If all the curves are plotted with the same ordinate for a particular voltage it will be seen that there is a greater approach to saturation in the curves (*b*) than in the curves (*a*). This may be partly due to the fact that the electrodes were 3·7 cm. apart for the curves (*a*), and only 0·7 cm. apart for the curves (*b*), but further observations with the electroscope show that this is not the full reason. Fig. 10 shows the form of curve obtained with the small currents observed just after the tube had been set up for use with the electroscope. They exhibited a tendency to curve in the opposite direction from the former curves. With the larger currents afterwards observed, curves similar to those in both figs. 9 (*a*) and 9 (*b*) were obtained. Fig. 11 (*a*) and (*b*) shows a series of such curves for ranges of



temperature 30° C. to 90° C. and 270° C. to 40° C. respectively. The distance between the electrodes was about 0·8 cm. in these experiments. The curves for 250° C. and upwards were measured by the galvanometer. In the case of the curves in fig. 11 (*b*) a magnification of that part of the curve near the origin, as in fig. 12, shows that there is a more or less sharp bend at under

4 volts potential difference. The currents were always immeasurable until a potential difference of about 0·9 volt was reached. So far as can be judged



from the record of the experiment, this sharp change in slope at less than 4 volts potential difference was only obtained after the potassium had been heated in the tube several times ; thus the state of the surface probably greatly affects the currents at low voltages.

It seems most probable that the real saturation current should thus be that for a small potential difference, and that the further increase is a super-saturation current due to some other cause. At high temperatures the cause must be chiefly impact ionisation. This view is confirmed by the fact that at a temperature of 270° C. (*cf.* curve for 269° C., fig. 11 (*b*)) a faint glow could be distinguished in the space between the electrodes when a potential difference of about 240 volts was applied, if the room was quite dark. Moreover, if a series of readings obtained at one time is plotted so that for a particular voltage

the ordinates coincide, as has been done in fig. 11 (*b*), it is generally found that the slope of the curve is smaller for a given voltage the higher the temperature. This would be brought about by the presence of a large number of positive ions formed by impact ionisation at higher temperatures. The increase of the current with voltage in fig. 10 is most probably due to impact ionisation, the true saturation current probably being very small.

The incomplete saturation was obtained even at room temperature. It is not likely that this was due to impact ionisation alone at such a low temperature, but to some other cause. The increase in current with voltage in this case might be due to the fact that electrons may be dragged away from the surface of the metal by the action of the field, an effect which has been investigated by W. Schottky.* Considering the effect of the external field (dV/dx) on the "image" force $\varepsilon^2/4x^2$ at a distance x from the surface Schottky finds that

$$\log_e i/S = \frac{\varepsilon^{\frac{3}{2}}}{kT}\sqrt{\frac{dV}{dx}}$$

where i = supersaturation current,
S = saturation current,
k = Boltzmann constant.

The ratio i/S should be larger the lower the value of the temperature T. Direct quantitative agreement with this relation was not obtained however. The effect is probably masked by the presence of others.

The Value of the Constants in the Emission Formula $i = A_1 \varepsilon T^{\frac{1}{2}} e^{-b/T}$.

By means of the relation (ii) between x and y, the values of b and A_1 can be calculated provided that the area a is known. An estimate of this quantity could be obtained by actual measurement in the various cases; its order of magnitude is all that is required to estimate A_1. The value of b is only affected by changes in the area during the measurements.

This was done for the readings obtained with the galvanometer for a potential difference of 370 volts. In each case a linear relation was found to hold, the slope corresponding very closely with the steepest part of the curves in fig. 7, for which the temperatures correspond to those for the galvanometer measurements. Table III below gives the calculated values of b and A_1 together with the diameter of surface D in centimetres and distance between the electrodes d in centimetres.

* 'Phys. Zeits.,' vol. 15, p. 872 (1914); *also* 'Jahrb. d. Rad. u. Elektronik,' vol. 12, p. 147 (1915).

Table III.

No.	$b \div 10^4$	D.	A_1	d.
1	1·39	0·7	$7 \cdot 5 \times 10^{22}$	3·2
2	1·30	0·7	$8 \cdot 9 \times 10^{21}$	3·2
3	1·42	0·7	$8 \cdot 6 \times 10^{22}$	3·5
4	1·37	0·7	$3 \cdot 8 \times 10^{22}$	3·7
5	1·41	0·7	$3 \cdot 1 \times 10^{23}$	—
6	1·22	1·7	$9 \cdot 8 \times 10^{20}$	1·0
7	1·15	1·7	$2 \cdot 7 \times 10^{20}$	1·0
8	1·15	1·7	$2 \cdot 0 \times 10^{20}$	1·0
9	1·30	1·7	$3 \cdot 6 \times 10^{21}$	1·0
10	1·24	1·7	$8 \cdot 1 \times 10^{20}$	1·0
11	1·35	1·7	$5 \cdot 6 \times 10^{21}$	1·0
12	1·21	—	—	—

Numbers 1 to 5 were obtained from the last five curves in fig. 3, the first two being irregular. The remaining numbers were obtained under very good vacuum conditions, the pressure being estimated at less than 10^{-6} mm., except for Number 11, for which it rose to 5×10^{-5} mm.

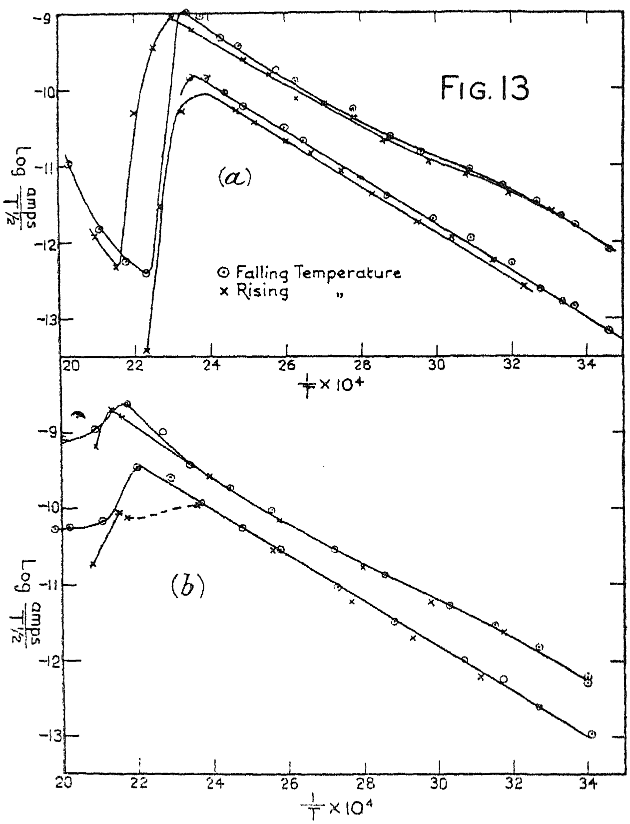
The values obtained from the curves for potential differences of 235 volts in fig. 7 depend on the particular temperature for which the slope is measured. Table IV gives the values calculated from these curves and others from the slope in the neighbourhood of 200° C. and 30° C. respectively.

Table IV.

	200° C.		30° C.	
	$b \div 10^4$	A_1	$b \div 10^4$	A_1
1. (Fig. 7 (*a*))	1·58	$3 \cdot 5 \times 10^{23}$	0·576	$3 \cdot 0 \times 10^{12}$
2. (Fig. 7 (*b*))	1·40	$9 \cdot 6 \times 10^{21}$	0·558	$3 \cdot 1 \times 10^{12}$
3. (Fig. 7 (*c*))	1·54	$2 \cdot 6 \times 10^{23}$	0·538	$3 \cdot 2 \times 10^{12}$
4.	1·32	$1 \cdot 4 \times 10^{22}$	0·502	$3 \cdot 0 \times 10^{11}$
5. (Fig. 15)	1·34	$1 \cdot 3 \times 10^{22}$	0·505	$4 \cdot 0 \times 10^{12}$
6.	1·30	$8 \cdot 9 \times 10^{21}$	0·528	$8 \cdot 3 \times 10^{12}$

The values for 30° C. should be more independent of complications due to the presence of potassium vapour, although even at these temperatures complete saturation was not obtained. To determine the effect of the potential difference on the slope of the curves, the current in a particular instance was measured in turn at 120, 235 and 350 volts potential difference as the temperature slowly fell. The three curves are shown in fig. 15, and are

practically parallel, so that so long as the potential difference is large, at least, the particular value has negligible effect on the slope. In view of the fact that in several cases an appearance of approximate saturation was observed for a potential difference of less than 4 volts, simultaneous measurements were made with potential differences of 4 and 235 volts. Two cases in which this was done are shown in figs. 13 (a) and (b). For these measurements the



tube had been re-set up and the reduction effect occurred at higher temperatures. Apart from this, the curves for 4 volts are perfectly straight, at least for values of $1/T \times 10^4$ greater than 24. The calculated values of b and A_1, which are given below in Table V, do not differ much on the whole from those for higher potential differences at the lower temperatures; they are slightly larger than the latter. Number 1, which is a good deal larger, was obtained when the potassium had been in the tube for eleven weeks and the currents at a particular temperature were smaller than those usually obtained. On taking the apparatus down after this set of readings it was seen that only a small

central portion of the surface was free from a coat of oxide or other solid matter.

Table V.

	$b \div 10^4$	A_1
1.	1·14	$2 \cdot 2 \times 10^{18}$
2.	0·707	$5 \cdot 4 \times 10^{15}$
3. (Fig. 13 (*a*))	0·689	$2 \cdot 6 \times 10^{15}$
4.	0·643	$1 \cdot 1 \times 10^{15}$
5.	0·681	$5 \cdot 6 \times 10^{15}$
6.	0·645	$7 \cdot 2 \times 10^{14}$
7. (Fig. 13 (*b*))	0·687	$2 \cdot 6 \times 10^{15}$
8.	0·807	$2 \cdot 1 \times 10^{15}$

A comparison of all the values of b quoted above with those yet obtained by various experimenters for other metals* shows that they are much smaller than the latter, while the values of A_1 are of a low order of magnitude. This will be discussed after the photo-electric measurements have been considered.

The Photo-electric Measurements.

In making a comparison between the thermionic and photo-electric work functions, it is advisable to make the measurements of both under the same conditions. Since the photo-electric currents obtained with monochromatic light were only measurable when the electroscope, or electrometer, was used without any additional capacity, to do this the potassium was raised to about 200° C. and allowed to cool while thermionic measurements were made, till it reached room temperature, when a photo-electric curve was taken using the illuminator. In many cases the thermionic current was not negligible even at this temperature, so its value was continually measured and subtracted from the total current obtained with the potassium illuminated. The potassium was then slowly heated, while further thermionic readings were taken. The pumps were kept running the whole time.

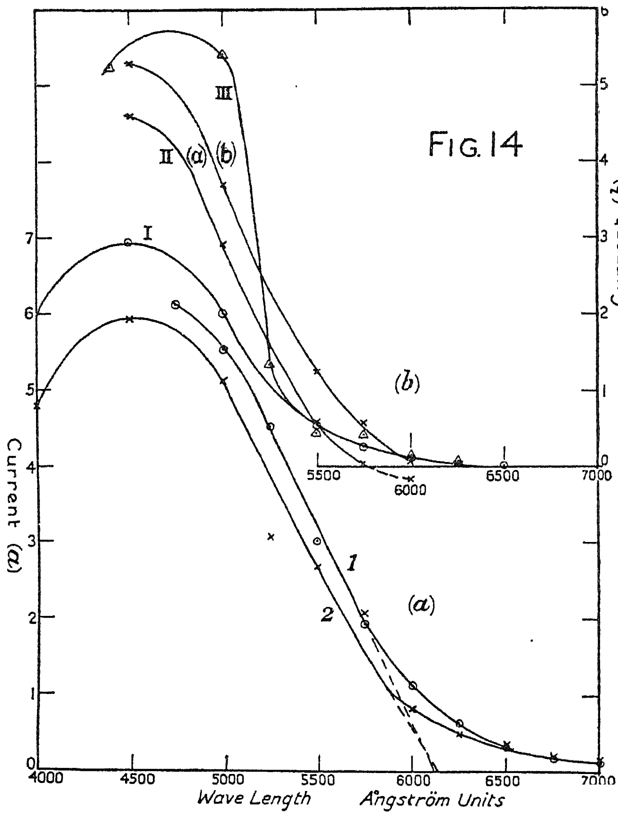
The current potential difference curves exhibited greater saturation at all temperatures than for the thermionic currents. Table VI and fig. 16 show the currents at 10 and 235 volts respectively for various temperatures when the concentrated beam from the Pointolite lamp was directed on to the surface through the window in the heater.

* *See* O. W. Richardson, 'Emission of Electricity from Hot Bodies,' p. 81 (1921).

Table VI.

Temperature (° C).	Current at 10 volts.	Current at 235 volts.
198	16·7	18·2
173	19·8	22·4
136	14·7	17·2
110	13·7	15·4
84	15·7	18·2
57	15·7	18·3
33	15·8	19·4
26	13·3	16·0

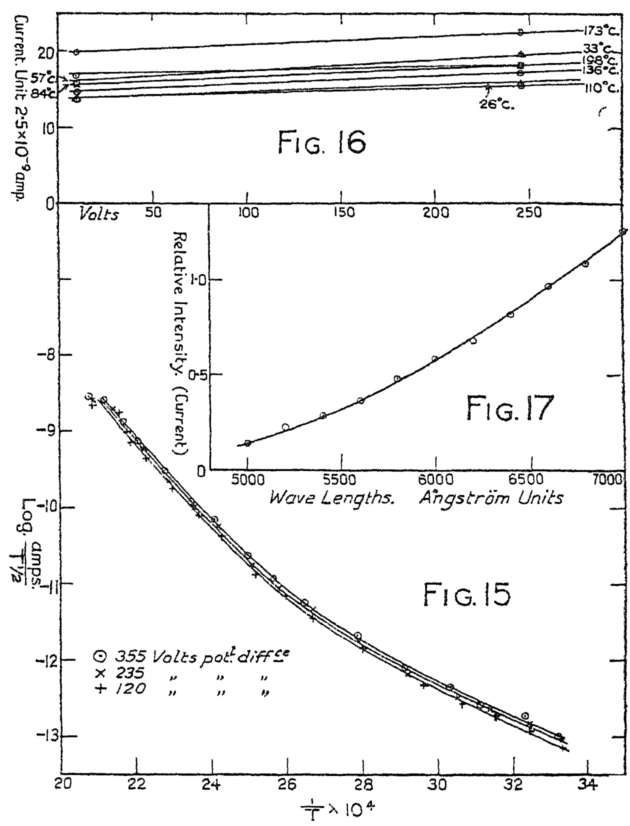
The photo-electric measurements showed that in all cases practically the whole of the electrons were liberated by light of wave-lengths between 3500 and 6500 Ångström units. Wave-lengths less than 3500, however, are largely absorbed by the glass bulb of the Pointolite lamp and the glass lens. Fig. 14 (*a*) shows two typical photo-electric curves. Number 1 was obtained between the taking of the readings for the two curves (*c*) in fig. 7, while Number 2



was obtained immediately after the curve for Number 6 in Table IV. The ordinates represent the currents obtained with 235 volts accelerating potential difference with light from the illuminator set to the wave-length represented as abscissa. The estimation of the threshold frequency is complicated by the fact that the curves approach the wave-length axis asymptotically. This effect may be either real or due to light of slightly shorter wave-lengths scattered by dust particles or parts of the apparatus. The relative energy of the incident light for different wave-lengths is shown in Table VII and fig. 17.

Table VII.

Wave-length (Ångström units).	Relative Intensity.	Wave-length (Ångström units).	Relative Intensity.
5000	0·14	6200	0·68
5200	0·22	6400	0·82
5400	0·28	6600	0·97
5600	0·36	6800	1·09
5800	0·48	7000	1·26
6000	0·58	—	—



It was obtained by fixing the linear thermopile intended for the infra-red spectrometer in position behind the slit and measuring the current through a sensitive galvanometer. The intensity rapidly increases with increasing wave-length to a maximum out in the infra-red. The various values of the threshold wave-length λ_0 which are obtained when the asymptotic part of the curve is neglected are given below in Table VIII under λ_0. The wave-lengths λ'_0, for which the photo-electric currents become immeasurable, are also given. The corresponding values ϕ_0 and ϕ'_0 of the work in equivalent volts necessary for the electron to escape from the surface with zero energy, calculated from the relation

$$\phi_0 \times 10^8 = \frac{h\nu_0}{\varepsilon} = \frac{hc}{\lambda_0\varepsilon},$$

are also given.

The value of h/ε was taken as $\dfrac{6 \cdot 55 \times 10^{-27}}{1 \cdot 591 \times 10^{-20}}$ erg sec. per E.M.U.

Table VIII.

No.	λ_0 (Å.u.)	ϕ_0 (volts).	λ'_0 (Å.u.)	ϕ_0' (volts).	Slit widths of illuminator (mm.).	Accelerating potential difference (volts).	Remarks.
1	6120	2·02	7000	1·77	0·08	235	Between readings for fig. 7 (c) (3, Table 4).
2	6140	2·01	7000	1·77	0·08	235	After readings for 6, Table 4.
3	6220	1·99	7200	1·72	0·08	10	Between readings 8, Table 5.
4	6640	1·86	7000	1·77	0·13	10	Between readings for 6, 7, Table 3.
5	6250	1·98	7000	1·77	(?)	(?)	Between readings for 8, 9 and 10, 11, Table 3.

With regard to the reduction in the magnitude of the thermionic current with increasing temperature, mentioned above, some photo-electric curves were obtained at the same time as the readings for fig. 6. They are shown in fig. 14 (*b*). Number I was obtained before the temperature of the potassium had been raised, Numbers II (*a*) and (*b*) when it had been raised so high that the current had again become very small, while No. III was obtained after the potassium had been allowed to cool again. The Numbers I, II, III in fig. 6 show the parts of the curves to which the photo-electric measurements refer. With the measurements II (*a*) and (*b*) the residual thermionic current had to be allowed for, and the measurements carried out rapidly, so that the

smallest currents could not be so accurately estimated. The accelerating potential difference was 235 volts and the slit widths of the illuminator 0·13 mm. At any rate, there was no marked falling-off of the photo-electric currents in the region for which they were a maximum, or any appreciable shift towards the ultra-violet which might be the result of an increase in the work necessary to send an electron through the surface.

Discussion of the Results.

There are several factors which might cause or affect the currents between the electrodes under the conditions of the experiment. These are namely :—

(1) Photo-electric action of traces of light ;

(2) Emission of positive ions from the potassium condensed on the central electrode ;

(3) Direct chemical reactions ;

(4) Ionisation in the space between the electrodes ;

(5) Evaporation of potassium.

The first may be definitely excluded as having negligible effect since the tube was enclosed in a dark box, and even when the currents were measured with the room quite dark at night time, they were still of the same order of magnitude. The second factor could not have had any large effect since, on the whole, there was no definite change in the magnitude of the emission, when all the potassium was kept off the platinum electrode (fig. 1 (*a*)) by glowing it when not taking a reading. The positive current from the main potassium surface was also quite negligible compared with the negative current at the same temperature. It was also found that the application of a suitable magnetic field by means of two coils completely stopped the current at room temperature, and reduced it to at least one-tenth of its value at temperatures of 190° C. The value of ε/m found when the distance between the electrodes was estimated approximately was also of the order of magnitude for the electron.

It is very unlikely that the thermionic currents were the result of direct chemical reaction of the residual gases.* The currents would be expected to be more variable in that case. Moreover, it would be expected that, if the currents at low temperatures were due to chemical action, they would continue to increase as the temperature was raised, instead of falling-off to a very low

* *Cf.* Haber and Just, 'Ann. d. Phys.,' vol. 36, p. 308 (1911); O. W. Richardson, 'Emission of Electricity from Hot Bodies,' 2nd Edit., p. 307 ; *ibid.*, 'Phil. Trans.,' A, vol. 222, p. 1 (1921).

value as they did in some cases. Also with sodium it was found that the current was immeasurable at temperatures at which Fredenhagen obtained considerable currents, even though there must have been still a considerable amount of gas absorbed in the metal. An experiment in which the potassium was maintained at about 53° C. with the pumps continually in action for ten hours showed that there was no appreciable falling-off of the currents with time.

The readings obtained at high temperatures are subject to the objection that the currents may be increased considerably, at high voltages at least, by impact ionisation. The effect of the latter must have been much smaller at temperatures just above that of the room. Even if we assume that the currents at high voltages are affected by impact ionisation or some other effect, the difference in the slopes at high and low voltages was quite small. The fifth factor ought not to have any large effect, since the currents appeared to vary independently of the evaporation of alkali metal which must have been continually taking place.

There are some other factors which might affect the observed currents. The currents were not found to be altered by cutting out the current through the heater. Also with the arrangement shown in fig. 1 (*b*) the application of a potential difference of 120 volts, positive or negative with respect to the central electrode, to the copper cylinder W, was found not to affect appreciably the current between the central electrode and potassium, even when the accelerating potential difference between the latter was only 120 volts. The measurement of temperature could not have involved serious error. It was found that the currents at a given temperature were approximately the same if the U part of the tube to within 0·5 cm. of the end of the copper cylinder W was surrounded by mercury in the iron heater, or the copper heater with the mica window was used. The thermometer assumed the temperature of the mercury very rapidly in the former case.

It will be seen from the values in Tables III, IV and V that b and A_1 are always low compared with the values yet obtained for other metals. These low values are still obtained when the currents are measured with small potential differences and at low temperatures, when complications due to impact ionisation should be less. The only exception to these low values was in the case of the curves shown in fig. 5, which refer to the small currents obtained just after the tube was set up. The values here, however, are possibly inaccurate, since the curves were not checked as the potassium cooled. If ϕ is the work done by an escaping electron in the thermionic emission

$$b = \phi/k.$$

or measuring ϕ in equivalent volts

$$\phi = \frac{bk \times 10^{-8}}{\varepsilon} = 0\cdot 86 \times 10^{-4} \,.\, b.$$

This will hold approximately so long as ϕ does not vary rapidly with T. The values of ϕ calculated from the values of b given in Tables III, IV and V are given below in Table IX, together with the photo-electric values ϕ_0 and ϕ'_0 from Table VIII in those cases to which they apply. The estimations of the photo-electric work function, even if we take the lower values ϕ'_0 obtained from the wave-length at which the current was almost immeasurable, are in all cases a good deal greater than the corresponding values of the thermionic

Table IX.

No.	Temp. 200° C.		Temp. 30° C.		Room Temp.	
	$b \div 10^4$	ϕ.	$b \div 10^4$	ϕ.	ϕ_0.	ϕ'_0.
	Table III—					
1.	1·39	1·19				
2.	1·30	1·12				
3.	1·42	1·22				
4.	1·37	1·18				
5.	1·41	1·21				
6.	1·22	1·05	—	—	1·86	1·77
7.	1·15	0·99	—	—		
8.	1·15	0·99	—	—		
9.	1·30	1·11	—	—	1·98	1·77
10.	1·24	1·06	—	—		
11.	1·35	1·16	—	—		
12.	1·21	1·04				
	Table IV—					
1.	1·58	1·36	0·576	0·495		
2.	1·40	1·20	0·558	0·480		
3.	1·54	1·32	0·538	0·463	2·02	1·77
4.	1·32	1·14	0·502	0·432		
5.	1·34	1·15	0·505	0·434		
6.	1·30	1·12	0·528	0·454	2·01	1·77
			Temps. 150–20° C.			
	Table V—					
1.	—	—	1·14	0·980		
2.	—	—	0·707	0·608		
3.	—	—	0·689	0·592		
4.	—	—	0·643	0·553		
5.	—	—	0·681	0·585		
6.	—	—	0·645	0·555		
7.	—	—	0·687	0·591		
8.	—	—	0·807	0·694	1·99	1·72

work function ϕ. The difference remains large, even when the values ϕ and ϕ_0 or ϕ'_0 are measured for practically the same temperatures and at the same time.

An explanation of this difference, suggested by Prof. O. W. Richardson, is that the thermionic current comes chiefly from those parts of the surface which have the smallest value of the work function, while the photo-electric current is more evenly distributed over the whole surface, a measurable amount coming also from those parts which have the higher values of the work function. That regions with extremely low values of the work function should exist is confirmed by the observations of J. Elster and H. Geitel,* and also of O. W. Richardson.† The former found that with a potassium photo-electric cell which had been made extremely sensitive by the action of an electrical discharge in hydrogen, measurable photo-electric currents were obtained with the radiation from an electric arc and a petroleum lamp, even through 0·97 mm. of ebonite, and also from a Nernst glower through 0·7 mm. of ebonite, well out in the infra-red region. There was no evidence to show that a definite wave-length existed at which the effect ceased. In the present experiment it is probable that traces of some hydrogen modification of the potassium surface existed, having an extremely low value of the work function, so that large numbers of electrons were emitted from these patches even at room temperature, since traces of hydrogen are difficult to remove from the alkali metals. Fredenhagen‡ also came to the conclusion that the currents he observed were probably due to hydrogen, which could be eliminated by long heating, although the protracted heating may have other effects as well as the elimination of hydrogen.

Such an explanation would account for the behaviour of the photo-electric and thermionic currents described in connection with fig. 11 (*b*), if the hydrogen modification were destroyed at higher temperatures by the evolution of gas from the copper cylinder or potassium itself, by the formation of a glow discharge, or simply by evaporation. It would also account for the smallness of the currents obtained on reversing the potential from the probably purer potassium condensed on the central electrode, and thus for the apparent contact potential difference to be observed in figs. 9 (*b*) and 12. The peculiar shape of the current-potential difference curves even at low temperatures might be accounted for by local fields set up by the electropositive patches. This

* J. Elster and H. Geitel, 'Phys. Zeits.,' vol. 12, p. 758 (1911).

† O. W. Richardson, 'Phil. Trans.,' A, vol. 222, p. 33 (1922).

‡ *Loc. cit.*

explanation will be reported on fully when further experiments on the action of hydrogen on potassium have been carried out.

These observations on the emission from potassium at temperatures down to that of the room confirm the observations of J. J. Thomson* and also of E. Müller,† and may account for a portion of the "Dunkeleffekt" observed by Elster and Geitel‡ with sensitive photo-electric cells.

In conclusion, I wish to thank Professor Richardson for suggesting this research and for supervising the experiments. The completion of this research has been assisted by a grant from the Radio Research Board of the Department of Scientific and Industrial Research, which the author gratefully acknowledges.

Summary.

1. Sodium was found not to give a measurable thermionic emission (*i.e.* greater than 10^{-10} amps.) for temperatures up to 390° C.

2. Potassium was found to give currents measurable in some cases by an electroscope at temperatures down to that of the room. The currents are believed to be of thermionic origin, and not due to chemical reaction. The values of b for potassium in the emission formula

$$i = A_1 \varepsilon T^{\frac{1}{2}} e^{-b/T}$$

were found lower than any others yet obtained with other metals, and the values of A_1 were also low.

3. The change of state of the potassium from solid to liquid or *vice versa* made no difference in the magnitude of the thermionic current or in the value of the constant b.

4. Determinations of the photo-electric work function ϕ_0 from photo-electric measurements, made at the same time as the thermionic measurements and at nearly the same temperature, showed that ϕ_0 was always a good deal greater than the thermionic work function ϕ calculated from the values of b.

5. An explanation of the observed effects, suggested by Professor O. W. Richardson, is given, which will be reported on more fully when further measurements have been made.

* J. J. Thomson, 'Phil. Mag.,' vol. 10, p. 584 (1905).

† E. Müller, 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 72 (1909).

‡ Elster and Geitel, 'Phys. Zeits.,' vol. 14, p. 741 (1913).

The Theoretical Scattering of Smoke in a Turbulent Atmosphere.

By O. F. T. Roberts, B.A.

(Communicated by Dr. G. C. Simpson, F.R.S. Received July 13, 1923.)

§ 1.—*Introductory.*

The fundamental result of G. I. Taylor's paper, "Eddy Motion in the Atmosphere,"* is that the scattering in a turbulent atmosphere of suspended matter, or diffusion of potential temperature, may be regarded as analogous to the diffusion of heat in a solid; on this theory every point in the atmosphere possesses a coefficient of eddy-diffusion, K, which may vary from point to point, and which may further differ for diffusion in different directions at any one point, analogous to the diffusion of heat in crystalline substances.

For the case in which K is the same at every point in the atmosphere the density of suspended matter, χ gms. per cm.^{3}, must satisfy the differential equation :—

$$\left(\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} + v\frac{\partial}{\partial y} + w\frac{\partial}{\partial z}\right)\chi = \mathrm{K}\nabla^2\chi, \tag{1}$$

where u, v, w are the components of mean velocity of the air.

The purpose of this paper is to obtain solutions of (1) applicable to several methods of artificial smoke production, viz.:

(A) A puff of smoke due to the instantaneous generation of matter at a point;

(B) A smoke-cloud produced continuously and uniformly at a fixed point in a uniform wind;

(C) A smoke-cloud produced continuously and uniformly along an unlimited straight line perpendicular to the direction of a uniform wind.

A theory of the optical opacity of smoke-clouds is then developed; an expression for the visible outline in terms of the density distribution is obtained, and is applied to cases (A) and (B) for an observer situated at a great distance across wind from the cloud. An extension of the above results to the case of K non-isotropic is then made. Diagrams illustrative of the above results are given.

§ 2.—*A Puff of Smoke.*

We take the origin of co-ordinates at the centre of the moving puff, x-axis down-wind, y-axis to left facing down-wind, z-axis vertically upwards; we

* 'Phil. Trans.,' A, vol. 215 (1915).

are justified in taking such moving axes, since the expansion of the puff is independent of the wind-velocity, the puff being merely carried bodily forward by the wind. Let Q grm. be the total mass of smoke instantaneously generated, and t be the time in seconds from the generation of the puff, then (1) becomes

$$\frac{\partial \chi}{\partial t} = \mathrm{K}\nabla^2\chi = \frac{\mathrm{K}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \chi}{\partial r}\right) \text{ for spherical symmetry,}$$

where, as usual, $r^2 = x^2 + y^2 + z^2$.

The solution which fits the conditions required, namely,

$$(a) \iiint_{-\infty}^{+\infty} \chi \, dx \, dy \, dz = \mathrm{Q},$$

$$(b) \ \chi = 0 \ \text{ for } t \to 0, \quad r \neq 0,$$

$$(c) \ \chi = 0 \ \text{ for } t \to \infty,$$

is

$$\chi = \frac{\mathrm{Q}}{8\,(\pi \mathrm{K}t)^{3/2}} e^{-r^2/4\mathrm{K}t} \tag{2}$$

[*see* Carslaw, 'Conduction of Heat,' 2nd Edn., p. 150.]

This may be written $r^2 = 4\mathrm{K}t \log \{\mathrm{Q}/8\chi\,(\pi \mathrm{K}t)^{3/2}\}$.

Whence it is easily deduced that a surface of density χ reaches a maximum radius of $\left\{\frac{3\mathrm{Q}^{2/3}}{2\pi e \chi^{2/3}}\right\}^{1/2}$ in a time $\frac{\mathrm{Q}^{2/3}}{4\pi e \chi^{2/3}\mathrm{K}} = \mathrm{T}_1$, say, and then falls to zero in a time $\mathrm{T}_2 = e \, . \, \mathrm{T}_1 = \frac{\mathrm{Q}^{2/3}}{4\pi \chi^{2/3}\mathrm{K}}$.

Thus $\qquad r^2 = 6\mathrm{K}t\,(\log \mathrm{T}_2 - \log t) = 6\mathrm{K}t\,(1 + \log \mathrm{T}_1 - \log t)$.

It is to be noticed that the maximum radius is independent of K.

This gives an approximation to the distribution of density within the puff due to an anti-aircraft shell-burst.

§ 3.—*A Smoke-Cloud produced continuously at a Fixed Point.*

Let q grm. per second be the rate of emission of matter at a fixed point, taken as the origin of co-ordinates.

Let Ox be the direction of the mean wind u cm./secs.

If P (x, y, z) be any point of the cloud, let angle PO$x = \theta$, OP $= r$, and the perpendicular from P on O$x = \varpi$.

If L be the projection of P on plane xOz, let OL $= \rho$, and angle L$Ox = \phi$. Thus $r^2 = x^2 + y^2 + z^2$, $\rho^2 = x^2 + z^2$, $\varpi^2 = y^2 + z^2$.

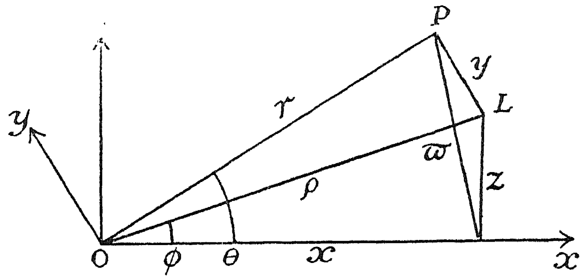


FIG. 1.

We suppose the emission to have been in progress for a period long enough for the density distribution to have reached a steady state: (1) then becomes

$$u\frac{\partial \chi}{\partial x} = K\nabla^2\chi.$$

For symmetry about Ox this becomes

$$\left(u \cos\theta \frac{\partial}{\partial r} - \frac{u \sin\theta}{r}\frac{\partial}{\partial \theta}\right)\chi = \frac{K}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial \chi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\chi}{\partial\theta}\right)\right].$$

We require a solution χ of this such that :—

(*a*) $\chi \to 0$ for $r \to \infty$, except perhaps for $\theta = 0$.

(*b*) $\chi \to \infty$ for $r \to 0$, and nowhere else.

(*c*) χ is such that the rate of transference of matter across a surface enclosing the origin is equal to q.

$$\chi = \frac{A}{r}e^{-\frac{ur}{2K}(1-\cos\theta)}$$

is found by substitution to be a solution of the differential equation; it also satisfies conditions (*a*) and (*b*).

For (*c*) we must use the following proposition :—

If fluid be moving in steady motion relative to fixed axes, velocity components at any point being (u, v, w); and if matter be present in the fluid of density χ at any point, the coefficient of diffusion of the matter being K; then the rate of transference of this matter across unit area of a surface, the direction cosines of whose normal $d\nu$ are (l, m, n), is

$$\chi(ul + vm + wn) - K\frac{\partial\chi}{\partial\nu}.$$

For $ul + vm + wn$ is the component of the velocity of the fluid across the

surface, and $-K\frac{\partial\chi}{\partial\nu}$ is, by definition of the diffusion coefficient, the rate of transference of matter by diffusion across unit area, when the fluid is at rest.

On applying this to a sphere of any radius described about the origin as centre, and equating to q the total rate of transference of particles across the sphere, we get :—

$$A = q/4\pi K.$$

Whence we obtain for the distribution of density in the cloud

$$\chi = \frac{q}{4\pi K r} e^{-\frac{ur}{2K}(1-\cos\theta)} \tag{3}$$

If we neglect 4th and higher powers of θ, as we may certainly do for points other than those in the immediate neighbourhood of the origin in the case of the elongated clouds produced by all but the lightest winds, (2) becomes

$$\left.\begin{aligned} \chi &= \frac{q}{4\pi K r} e^{-\frac{u\varpi^2}{4Kr}}, \\ \text{which may be written} \qquad \varpi^2 &= \frac{4K}{u}\left(\log\frac{q}{4\pi K\chi} - \log r\right) \end{aligned}\right\} \tag{4}$$

The following results may at once be deduced from (4) :—

The variation of density across wind is according to the Normal Law of Errors, being given by $e^{-u\varpi^2/4Kr}$; this affords a method of testing the theory, and of calculating K from cross-wind measurements of smoke density.

For $\varpi = 0$, $\chi = q/4\pi Kr$, showing that the density at any point along the axis of x varies inversely as the distance from the origin; it should be noted that this is independent of u.

The surface of density χ attains a maximum width $2\left(\frac{q}{u\chi\pi e}\right)^{1/2}$, independent of K, at a distance $\frac{q}{4\pi K\chi e} = d_1$, say, from the origin, and extends to a distance $d_2 = e \, . \, d_1$, from the origin. This means further that if the rate of emission does not exceed q, the concentration at a distance r cannot exceed $q/4\pi Kr$, however long the emission lasts.

§ 4.—*A Smoke-Cloud produced continuously along a Straight Line Perpendicular to the Wind.*

Let the rate of emission be q grm. per centimetre per second, and the source of emission be the axis of y, Ox being the direction of the mean wind, u cms./sec.

From the previous section the density distribution due to $q\,dy'$ at the point $(O\,.\,y'\,.\,O)$ is

$$d\chi = \frac{q\,dy'\,e^{-\frac{u}{2K}\left\{[\rho^2+(y-y')^2]^{\frac{1}{2}}-x\right\}}}{4\pi K\,\{\rho^2+(y-y')^2\}^{1/2}}.$$

The density, then, due to an infinite line source along the y-axis is obtained by integrating above from $-\infty$ to $+\infty$ for y'.

Using the transformation $y - y' = \rho \sinh \eta$, this gives

$$\chi = \frac{qe^{ux/2K}}{2\pi K}\int_0^\infty e^{-\frac{u\rho}{2K}\cosh\eta}\,d\eta.$$

But

$$\int_0^\infty e^{-\frac{u\rho}{2K}\cosh\eta} = K_0\left(\frac{u\rho}{2K}\right)$$

where $K_0(\lambda)$ is Bessel's Modified Function of the 2nd Kind and Zero Order, using notation of Whittaker and Watson's 'Modern Analysis.'

The asymptotic expansion of $K_0(\lambda)$ is

$$\left(\frac{\pi}{2\lambda}\right)^{1/2} e^{-\lambda}\left[1+\sum_{p=1}^{p=\infty}\frac{(-1)(-3^2)\ldots(-\overline{2p-1}^2)}{\lfloor p\, 2^{3p}\lambda^p}\right]$$

$$= \left(\frac{\pi}{2\lambda}\right)^{1/2} e^{-\lambda}\left\{1-\frac{1^2}{8\lambda}+\frac{1^2 3^2}{1\,.\,2\,.\,(8\lambda)^2}-\ldots\right\}.$$

Replacing λ by $u\rho/2K$, and substituting likely values of K and u, shows that even quite moderate values of ρ will make the ratio $1/8\lambda$ small enough to be unimportant (*e.g.* $K < 10^5$, $u > 10^3$, $\rho > 10^3$).

In practice, then, a sufficient accuracy is obtainable by omitting all but the first term of the asymptotic expansion. This gives the approximation

$$\chi = q\,\frac{e^{ux/2K}}{2\pi K}\left(\frac{\pi}{u\rho/K}\right)^{1/2} e^{-\frac{u\rho}{2K}}.$$

Therefore

$$\chi = \frac{qe^{-\frac{u\rho}{2K}(1-\cos\phi)}}{2\pi^{\frac{1}{2}}K^{\frac{1}{2}}u^{\frac{1}{2}}\rho^{\frac{1}{2}}}. \tag{5}$$

This leads by a further approximation, neglecting 4th and higher powers of ϕ, to

$$\chi = \frac{qe^{-\frac{uz^2}{4K\rho}}}{2\pi^{\frac{1}{2}}K\,u^{\frac{1}{2}}\rho^{\frac{1}{2}}}$$

which may be written

$$z^2 = \frac{2K\rho}{u}\left(\log\frac{q^2}{4\pi K u N^2} - \log\rho\right)\,.\,. \tag{6}$$

From (6) the following may be deduced :—

The variation of density in the vertical direction is, according to the Normal Error Law, being given by $e^{-uz^2/4K\rho}$.

$$\text{For} \qquad z = 0, \qquad \chi = \frac{q}{2\pi^{\frac{1}{2}}K^{\frac{1}{2}}u^{\frac{1}{2}}\rho^{\frac{1}{2}}},$$

showing that the density at any point in xOy plane varies inversely as the square root of its distance from Oy.

The surface of density χ attains a maximum height from xOy plane, $\dfrac{q}{2^{\frac{1}{2}}\pi^{\frac{1}{2}}e^{\frac{1}{2}}uN}$ at a distance $\dfrac{q^2}{4\pi KuN^2e} = D_1$, from Oy, and extends to a distance $D_2 = e\,.\,D_1$ from Oy. This maximum width is noticeable for the absence of K.

§ 5.—*Investigation of Opacity.*

In the case of the scattering of certain forms of matter in the atmosphere we obtain the phenomenon of the obscuring of objects from an observer by means of the intervening scattered matter. A detailed, quantitative, theoretical or experimental investigation of the physical causes of the obscuring of an object from an observer by intervening smoke has not yet been made; the result would certainly be dependent on certain physiological factors (*e.g.*, the swamping of the light, entering the eye from the object viewed, by light reflected from particles of smoke in the near neighbourhood of the line of vision).

For the purpose of obtaining some idea of the apparent shape of the clouds of smoke produced by the methods investigated in §§ 2 and 3 above, the following approximate theory is suggested.

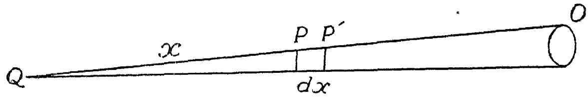


FIG. 2.

Let Q be a point of an object viewed from O; and let the pupil of the observer's eye at O (or lens of camera) subtend a solid angle ω at Q. Let I be the intensity at distance QP $= x$ cms. from Q of the light from Q. Let n be the number of smoke particles per cm.^{3} at P, and A their average cross-sectional area at P.

Then, considering the loss of intensity in passing from P to P′, a distance

dx, and supposing that the smoke particles produce loss of intensity by screening only, we get :—

$$Ix^2\omega = \left(I + \frac{\partial I}{\partial x} . dx\right)(x + dx)^2 \omega + I . Anx^2\omega\, dx,$$

giving
$$\frac{\partial I}{\partial x} = - I\{An + 2/x\}.$$

Therefore
$$I = \frac{I_a a^2 e^{-\int_a^x Anx}}{x^2}$$

where $I = I_a$ for $x = a$.

We will consider only the case of A constant: this amounts to supposing that samples taken at any portion of the cloud will contain the same proportion of particles of different sizes.

This gives
$$I = \frac{I_a a^2 e^{-A\int_a^x n\,dx}}{x^2}.$$

But $\int_a^x n\,dx$ is the number of particles in a tube of unit cross-section along QO between distances a and x from Q. We assume that the definition of an object is just obscured if the light-intensity from it has fallen to a certain fraction λ of what it would be in the absence of intervening smoke.

Thus $\lambda = e^{-A\int_Q^O n\,dx}$ if QO passes through the apparent outline of the cloud as viewed from O. This gives $-\log \lambda/A = \int_Q^O n\,dx = N$, say.

The number N, then, so defined, is the number of particles in a tube of unit cross-section through the observer, necessary to obtain obscuring of the background.

Assuming this theory, the apparent shape of any cloud of smoke as viewed from any point of observation may be obtained if the distribution of density χ (particles per cm.^{3}, rather than grams per cm^3.) is known, and also the constant N.

This will now be applied to the outlines of a smoke puff as viewed by a distant observer, and of a cloud produced by continuous emission from a point as viewed by a distant observer in a direction perpendicular to the wind velocity.

§ 6.—*Outline of a Puff of Smoke.*

The expression for the density given by equation (2) is :—

$$\chi = \frac{Q}{8\,(\pi K t)^{3/2}}\, e^{-r^2/4Kt}.$$

The outline, then, as viewed by a distant observer in the direction Oy, is given by,

$$\left.\begin{aligned} N &= \int_{-\infty}^{+\infty} \chi\, dy \\ &= \frac{Q}{8\,(\pi K t)^{3/2}} \int_{-\infty}^{+\infty} e^{-(\rho^2+y^2)/4Kt}\, dy \\ &= \frac{Q e^{-\rho^2/4Kt}}{4\pi K t} \\ \text{or} \qquad \rho^2 &= 4Kt\,\{\log Q/4\pi K N - \log t\}. \end{aligned}\right\} \qquad (7)$$

Whence it is easily deduced that the outline reaches a maximum radius of $\left(\frac{Q}{\pi N e}\right)^{1/2}$, independent of K, in a time $Q/4\pi K N e = t_1$, say, and then falls to zero in a time $t_2 = e\,.\,t_1 = Q/4\pi K N$.

Observations of the expansion with time of an anti-aircraft shell-burst may be compared with the theoretical value for the radius given by

$$\rho^2 = 4Kt\,\{\log t_2 - \log t\},$$

thus testing the theory and obtaining a measure of K at considerable heights above the earth's surface.

§ 7.—*Outline of a Smoke-Cloud produced continuously at a Point.*

The expression for the density given by equation (3) is

$$\chi = \frac{q}{4\pi K}\, e^{-\frac{ur}{2K}(1 \cos\theta)}.$$

The outline, then, as viewed by a distant observer in the direction Oy, is given by :—

$$N = \int_{-\infty}^{+\infty} \chi\, dy = \frac{q e^{ux/2K}}{4\pi K} \int_{-\infty}^{+\infty} \frac{e^{-\frac{u}{2K}\{(\rho^2+y^2)^{\frac{1}{2}}\}}}{(\rho^2+y^2)^{\frac{1}{2}}}\, dy.$$

The analysis is identical with that of § 4 (for production of smoke from a uniform line source), and to the same degree of approximation leads to :—

$$\left.\begin{aligned} N &= \frac{q e^{-\frac{uz^2}{4K\rho}}}{2\pi^{\frac{1}{2}} K^{\frac{1}{2}} u^{\frac{1}{2}} \rho^{\frac{1}{2}}} \\ \text{or} \qquad z^2 &= \frac{2K\rho}{u}\{\log q^2/4\pi K u N^2 - \log \rho\}. \end{aligned}\right\} \qquad (8)$$

We get from this that the outline attains to maximum width $2^{1/2}q/\pi^{1/2}e^{1/2}u\mathrm{N}$, independent of K_1 at a distance $q^2/4\pi \mathrm{K}u\mathrm{N}^2e = \mathrm{D}_1$, from the point of emission, and that the total apparent length is $\mathrm{D}_2 = e \,.\, \mathrm{D}_1$.

§ 8.—*Extension of above Results to the Case of K Non-isotropic.*

In the region close to the ground it is probable that the eddy-diffusion is not the same in different directions; it seems reasonable in this case to take the directions, down-wind, cross-wind, and vertical as the "principal directions" of diffusion.

The differential equation to be satisfied by the density χ is then,

$$\left(\frac{\partial}{\partial t} + u\frac{\partial}{\partial x}\right)\chi = \left(\mathrm{K}_1\frac{\partial^2\chi}{\partial x^2} + \mathrm{K}_2\frac{\partial^2\chi}{\partial y^2} + \mathrm{K}_3\frac{\partial^2\chi}{\partial z^2}\right), \qquad (1')$$

where K_1, K_2, K_3 are non-zero constants.

Transferring to a $\xi\eta\zeta$ space defined by

$$\frac{x}{\mathrm{K}_1^{1/2}} = \frac{\xi}{(\mathrm{K}_1\mathrm{K}_2\mathrm{K}_3)^{1/6}}, \text{ etc.,}$$

we get $dx\, dy\, dz = d\xi\, d\eta\, d\zeta$,

and
$$\frac{u}{\mathrm{K}_1^{1/2}} = \frac{\mathrm{U}}{(\mathrm{K}_1\mathrm{K}_2\mathrm{K}_3)^{1/6}}$$

where U is velocity in $\xi\eta\zeta$ space corresponding to u.

Hence density χ at (x, y, z) transfers to the same density χ at $(\xi\eta\zeta)$.

The equation (1′) becomes :—

$$\mathrm{U}\frac{\partial\chi}{\partial\xi} + \frac{\partial\chi}{\partial t} = (\mathrm{K}_1\mathrm{K}_2\mathrm{K}_3)^{1/3}\left\{\frac{\partial^2\chi}{\partial\xi^2} + \frac{\partial^2\chi}{\partial\eta^2} + \frac{\partial^2\chi}{\partial\zeta^2}\right\}.$$

The solution of (1′) reduces thus to the solution of an equation of form of equation (1) in the $\xi\eta\zeta$ space.

The results obtained by applying this method are as follows :—

For a puff of smoke produced instantaneously,

$$\chi = \frac{\mathrm{Q}e^{-\left\{\frac{x^2}{4\mathrm{K}_1} + \frac{y^2}{4\mathrm{K}_2} + \frac{z^2}{4\mathrm{K}_3}\right\}\frac{1}{t}}}{8\,(\pi t)^{3/2}\,(\mathrm{K}_1\mathrm{K}_2\mathrm{K}_3)^{1/2}}. \qquad (2')$$

Apparent outline of puff of smoke viewed from direction $\mathrm{O}y$ is given by :—

$$\mathrm{N} = \frac{\mathrm{Q}e^{-\left(\frac{x^2}{4\mathrm{K}_1} + \frac{z^2}{4\mathrm{K}_3}\right)\frac{1}{t}}}{4\pi t\,(\mathrm{K}_1\mathrm{K}_3)^{1/2}}. \qquad (7')$$

For smoke produced continuously at a point in a wind of velocity u

$$\chi = \frac{q e^{-\frac{u}{2K_1^{\frac{1}{2}}}\left\{\left(\frac{x^2}{K_1}+\frac{y^2}{K_2}+\frac{z^2}{K_3}\right)^{\frac{1}{2}}-\frac{x}{K_1^{\frac{1}{2}}}\right\}}}{4\pi\{K_1K_2K_3\}^{\frac{1}{2}}\left\{\frac{x^2}{K_1}+\frac{y^2}{K_2}+\frac{z^2}{K_3}\right\}^{\frac{1}{2}}}. \tag{3'}$$

If we may neglect $\dfrac{y^2/K_2+z^2/K_3}{x^2/K_1}$ this becomes :—

$$\chi = \frac{q e^{-\frac{u}{4x}\left(\frac{y^2}{K_2}+\frac{z^2}{K_3}\right)}}{4\pi(K_2K_3)^{1/2}x}, \tag{4'}$$

which is independent of K_1.

Apparent outline of a cloud of smoke produced continuously at a fixed point, viewed from direction Oy, is given by

$$N = \frac{q e^{\frac{ux}{2K_1}}}{2\pi(K_1K_3)^{1/2}} K_0 \left\{ \frac{u\left(\frac{x^2}{K_1}+\frac{z^2}{K_3}\right)^{1/2}}{2K_1^{1/2}} \right\}, \text{ exactly,}$$

or

$$N = \frac{q e^{-\frac{uz^2}{4xK_3}}}{2\pi^{\frac{1}{2}}u^{\frac{1}{2}}K_3^{\frac{1}{2}}x^{\frac{1}{2}}} \text{ approximately,} \tag{8'}$$

which is independent of K_1 and K_2.

Deductions as regards length of cloud, maximum width, etc., similar to those for K isotropic, are obtainable from above equations.

§ 9. Any experimental test of these theoretical results is difficult, owing to the fact that K and u are both functions of z, varying with height, at any rate in the neighbourhood of the ground. This does not apply so much, however, to the isolated puff, as represented by an anti-aircraft shell-burst ; in which case, however, any density measurements are out of the question, and to obtain any results to compare practice and theory, the more doubtful optical result, equation (7), must be applied.

It should be pointed out that as the use of K, the coefficient of eddy-diffusion, is only justified as a result of averaging over some definite time, so the values of density here obtained are only average values, the actual density at any point within a cloud varying, in an oscillatory manner, with the passage of patches of air impregnated with greater or less concentrations of smoke. Since this averaging must take place over a long time compared to the passage of a single whorl of smoke, the above results will agree, it seems, least with the actual phenomena, where the linear dimensions of the cloud are of the same order as those of the whorls ; that is to say, in the neighbourhood of the point of emission, or the initial stages of the expansion of the puff.

§ 10.—*Diagrams Illustrating above Results.*

The accompanying diagrams illustrate the results for continuous emission from a point source. Diagrams A, B, C show sections by a plane through Ox of a surface of equal density ; equation (4).

A shows effect of varying χ/q only.
B ,, ,, u ,,
C ,, ,, K ,,

A_1, B_1, C_1 are identical.

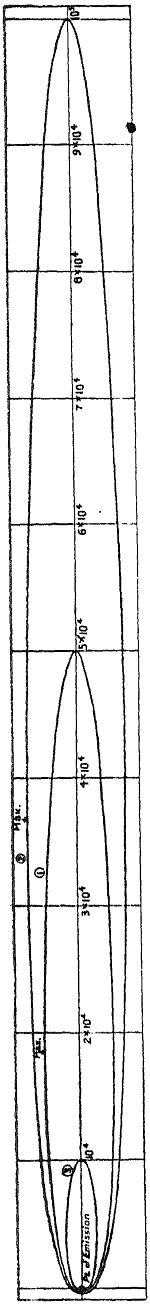
The values of the constants are given in the following table :—

Diagram	No.	K	u	χ/q	Consequent value of d_2.
A	1	10^4	10^2	$\dfrac{1}{2\pi . 10^9} = \mu$	5×10^4
	2	10^4	10^2	$\frac{1}{2}\mu$	10^5
	3	10^4	10^2	5μ	10^4
B	1	10^4	10^2	μ	5×10^4
	2	10^4	3×10^2	μ	5×10^4
	3	10^4	10^3	μ	5×10^4
C	1	10^4	10^2	μ	5×10^4
	2	3×10^4	10^2	μ	$\frac{5}{3} \times 10^4$
	3	10^5	10^2	μ	5×10^3

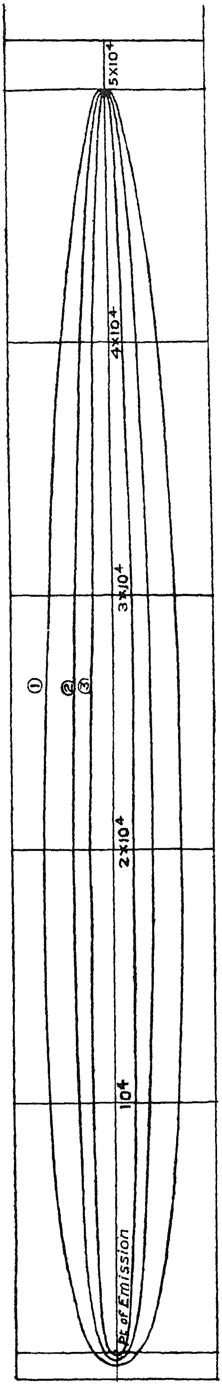
D shows the outline when u is varied ; equation (8) ; the constants being as in the following table :—

Diagram	No.	K	u	N^2/q_2	Consequent value of D_2.
D	1	10^4	10^2	$1/2\pi . 10^{11}$	5×10^4
	2	10^4	3×10^2	,,	$\frac{5}{3} \times 10^4$
	3	10^4	10^3	,,	5×10^3

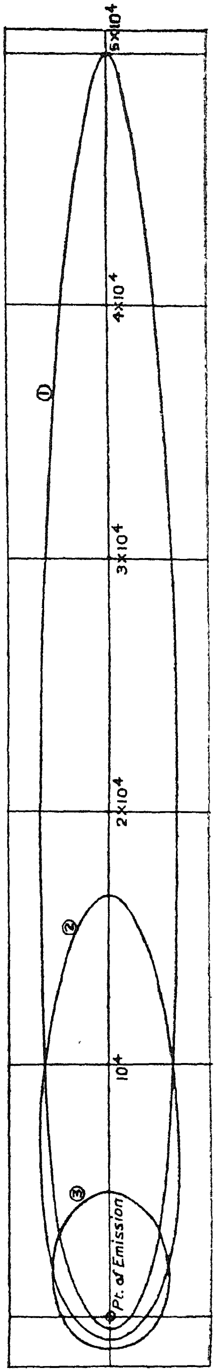
The variation of the outline when N^2/q^2 or K are varied is of the same nature as the variation illustrated in diagrams A and C above.



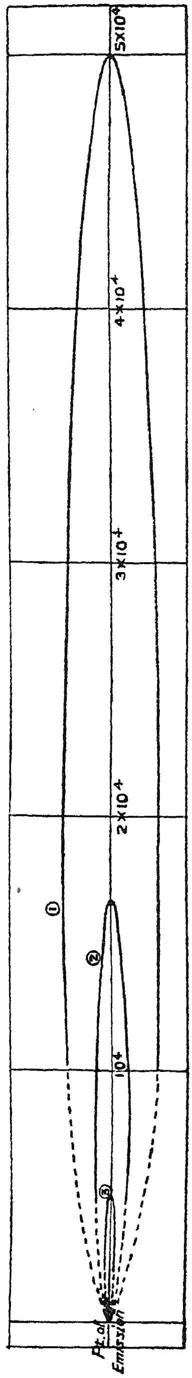
A. χ/q varied. (Scale 1/6000.)



B. u varied. (Scale 1/3000.)



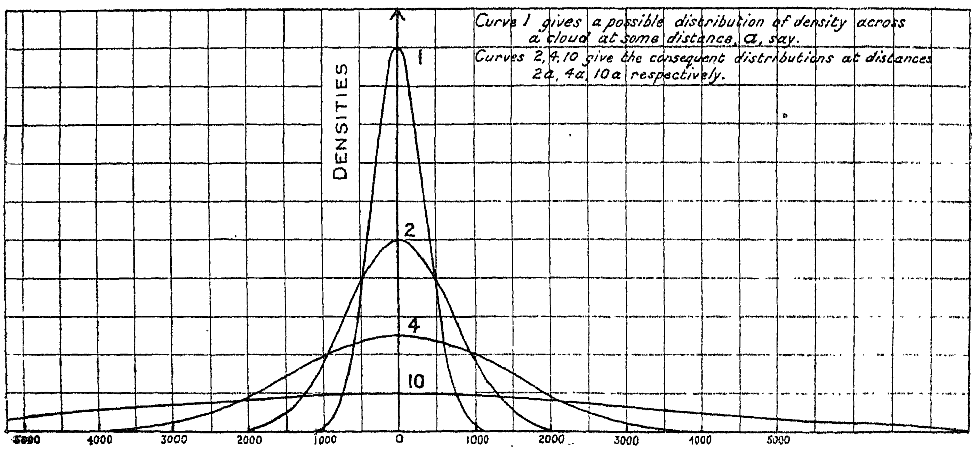
C. K varied. (1/3000.)



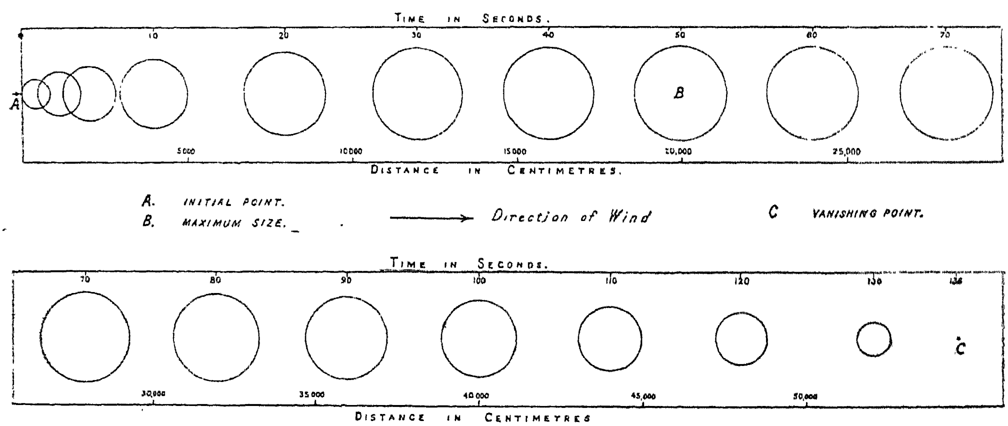
D. u varied (1/3000.)

Diagram E shows a different way of illustrating equation (4), indicating the variation in the cross-wind density distribution relation as we proceed down-wind.

Diagram F shows the apparent expansion and contraction of a puff of smoke produced instantaneously, illustrating equation (7), the constants being, $K = 10^4$, t_1 (time to maximum expansion) $= 50$ seconds.



E. Illustrating Equation (4).



F. Apparent size of smoke puff. Wind 400 cm./sec.

Note.—The following are some observations on two anti-aircraft shell-bursts, which are compared with the theoretical expression for the expansion of a puff of smoke.

The diameters of the smoke-puffs were obtained photographically with a long-focus camera, the distance of the puffs from the camera being computed

from the rectangular co-ordinates of the puff given by the "Mirror" method, due to Professor A. V. Hill, F.R.S.

If t is the time from burst, t_2 the total time of existence of the puff, and d the apparent diameter, the preceding theory gives the relation,

$$d^2 = 16\mathrm{K}t\,\{\log_e t_2 - \log_e t\}.$$

Clearly if we plot d^2/t against $\log_e t$ the points obtained should, if the observations are at all in accordance with the theory, lie along a straight line, the tangent of whose slope gives 16K.

Owing to the slight irregularity in the outline of the puffs d^2 is taken as the mean square diameter of the puff, measured horizontally and vertically from the point of view of the observer.

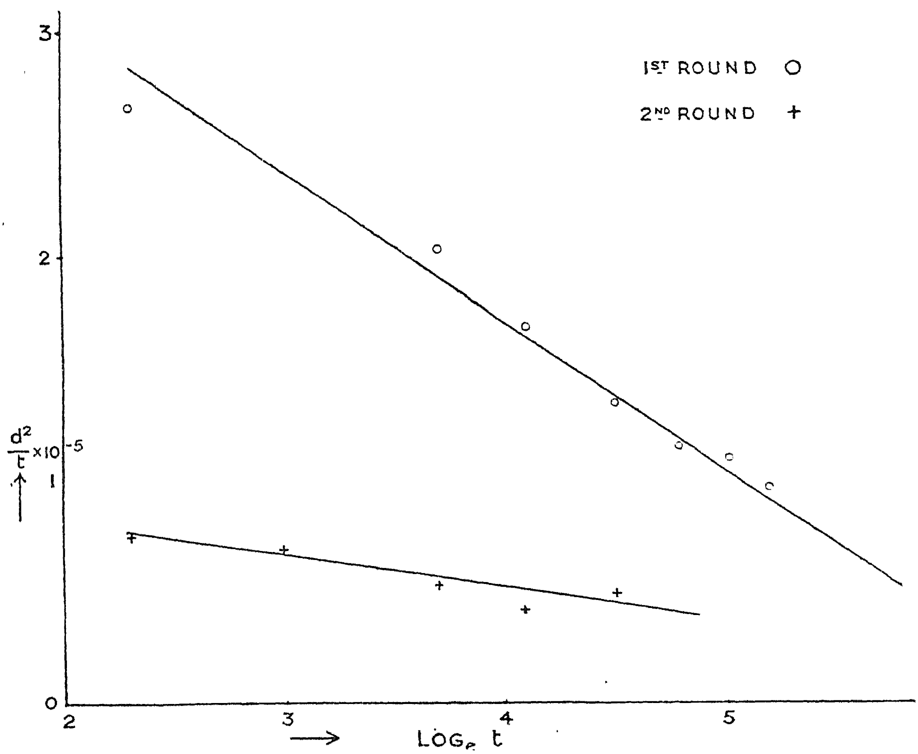


FIG. 3.

The figure shows $d^2/t \times 10^{-5}$ plotted against $\log_e t$.

		cm.²/second.		
	$\log_e t$	d^2/t for Rd. 1.	d^2/t for Rd. 2.	
10	2·30	$2 \cdot 66 \times 10^5$	$0 \cdot 75 \times 10^5$	
20	2·99	—	$0 \cdot 69 \times 10^5$	
40	3·69	$2 \cdot 03 \times 10^5$	$0 \cdot 53 \times 10^5$	
60	4·09	$1 \cdot 68 \times 10^5$	$0 \cdot 42 \times 10^5$	
90	4·50	$1 \cdot 35 \times 10^5$	$0 \cdot 49 \times 10^5$	
120	4·79	$1 \cdot 16 \times 10^5$		
150	5·01	$1 \cdot 10 \times 10^5$		
180	5·19	$0 \cdot 97 \times 10^5$		

Round 1 is at a height of 5300 metres.
Round 2 ,, ,, 2450 ,,

The optimum straight line is drawn for each round; it is seen that the points do not lie materially off a straight line. The calculations of K from the slopes of the lines gives

$$\text{Round 1, } K = 0 \cdot 41 \times 10^4.$$
$$\text{Round 2, } K = 0 \cdot 094 \times 10^4.$$

These results are not, of course, sufficient to verify even a portion of the preceding theory; but they certainly give an idea of the order of the value of K to be expected at such heights.

Studies in Brownian Movement.—II. The Determination of Avogadro's Number from Observations on Bacteria (Cocci).

By John H. Shaxby, Viriamu Jones Physical Laboratory, University College, Cardiff.

(Communicated by Prof. S. W. J. Smith, F.R.S. Received Sept. 20, 1923.)

1. The Brownian movement is now definitely accepted as a manifestation of the motion of molecules in the fluid state. Its mathematical theory, first given by Einstein*, has been verified by Perrin and his co-workers† for liquid media, by Harvey Fletcher‡, Eyring§ and others for gases.

The most usual form of the equation of Brownian movement is

$$\overline{l^2} = \frac{\mathrm{RT}}{\pi \mathrm{N} \eta a} t,$$

in which R is the gas constant and N the number of molecules per gram-molecule of a perfect gas, T the absolute temperature and η the viscosity of the medium which suspends spherical particles exhibiting the movement, a the radius of such a particle and $\overline{l^2}$ the mean square of its displacement in a time t, this displacement being wholly due to the Brownian movement.

The same equation has been derived in other ways by Smoluchowski (with a changed numerical factor)||, by Langevin¶ and by Einstein and Hopf**.

For purposes of experiment the quantity observed is not $\overline{l^2}$ but $\overline{x^2}$, the mean square of the displacement in some chosen direction, *e.g.*, a horizontal line parallel to the length of a micrometer scale. The random nature of the movements immediately gives the equation

$$\overline{x^2} = \frac{\mathrm{RT}}{3\pi \mathrm{N} \eta a} t, \qquad (a)$$

or if, instead of the mean square of the displacement, we employ simply the mean displacement $\bar{r}$, then

$$(\bar{r})^2 = \frac{2\mathrm{RT}}{3\pi^2 \mathrm{N} \eta a} t. \qquad (b)$$

* 'Ann. d. Physik,' vol. 19, p. 371 (1906).

† Numerous papers in 'C.R.' from 1908 onwards.

‡ 'Phys. Rev.,' vol. **33**, p. 81 (1911); 2nd Ser., vol. 4, p. 440 (1914).

§ 'Phys. Rev.,' 2nd Ser., vol. 5, p. 412 (1915). See also Schidlof and Targonski, 'C.R.,' vol. 162, p. 788 (1916), and Schmid 'Akad. Wiss. Wien,' vol. 129, p. 813 (1920).

|| 'Ann. d. Physik,' vol. 21, p. 756 (1906).

¶ 'C.R.,' vol. 146, p. 530 (1908).

** 'Ann. d. Physik,' vol. 33, p. 1105 (1910).

2. The equation may also be derived by the following method, which has the advantage of bringing out clearly the physical processes involved.

A suspended particle undergoes impacts from molecules of the suspending fluid. Each of these impacts causes a change in its momentum, but as there is no regularity of any kind in the blows the short rectilinear paths between successive collisions make up a quite irregular zig-zag track. We may introduce simplification by supposing the particle to move along this track always with the same speed G, the root-mean-square velocity appropriate to its mass at the given temperature, and thus to undergo irregular changes in direction only.

Consider a particle of mass m at a point 0 at a given instant to be moving in direction OA. In time this particle will lose all its velocity in this direction. *i.e.*, it will be moving with speed G in a direction perpendicular to OA. Let the mean interval of time for this change to come about be t_1. It is Smoluchowski's "Relaxation Time." The total impulse necessary to maintain the velocity G during the time t_1 is $6\pi\eta a G t_1$, by the law of Stokes. The momentum destroyed is mG. Hence $6\pi\eta a t_1 = m$, or $t_1 = m/6\pi\eta a$ ....(1)

The actual change of momentum in the time t_1 is $\sqrt{2}\, m\mathrm{G} = \mu_1$ ....(2)

We may then regard this interval of time t_1, the period during which, on the average, a particle loses all its momentum in an assigned direction, as a sort of natural unit for the phenomena we are considering.

Now Lord Rayleigh* has shown in papers on Random Flights that the mean value of the resultant of a large number n of vectors, all equal in magnitude but completely random in direction, is defined by the equation $\overline{\mathrm{P}^2}/n =$ constant, where $\overline{\mathrm{P}^2}$ is the mean value of the square of this resultant.

The separate rectilinear paths of Brownian movement are not such random vectors, because the direction of any one path is influenced by the directions of previous paths; but the successive increments of momentum satisfy the conditions, with the simplification we have made as to constancy of speed.

So $\overline{\mu^2}/t = \mu_1{}^2/t_1$, where $\overline{\mu^2}$ is the mean square of the momentum added in any time t, $\mu^2{}_1$ that for the particular time t_1.

But $\mu = 6\pi\eta\, al$, so $\overline{\mu^2} = (6\pi\eta a)^2\overline{l^2}$.

Substituting the values of t_1 and μ_1 from (1) and (2)

$$\frac{(6\pi\eta a)^2\,\overline{l^2}}{t} = \frac{2m^2\mathrm{G}^2}{t_1} = 2m\mathrm{G}^2 6\pi\eta a,$$

therefore
$$\frac{\overline{l^2}}{t} = \frac{m\mathrm{G}^2}{3\pi\eta a} = \frac{\mathrm{RT}}{\mathrm{N}\pi\eta a},$$

which is our equation of the Brownian movement.

* 'Collected Papers,' vol. 6, p. 604.

It is interesting to find the order of magnitude of the time interval t_1 the time in which a particle, on the average, loses its momentum in an assigned direction. For the particles of gamboge (density $1 \cdot 194$) used by Perrin, the radii varied between $0 \cdot 2\mu$ and $0 \cdot 5\mu$; the corresponding masses are 4×10^{-14} gm. and 60×10^{-14} gm. For water as the suspending medium this gives $1 \cdot 1 \times 10^{-8}$ seconds and $6 \cdot 4 \times 10^{-8}$ seconds as the values of t_1.

In work with gases a factor k has to be introduced into the calculations, because the mean free path is no longer small compared with the radius of a particle*, and the law of Stokes thus needs correction, taking the form $F = 6\pi\eta akv$, where F is the force needed to urge the particle with speed v. Hence the Brownian movement equation becomes $\overline{l^2} = RTt/N\pi\eta\, ak$, and the time $t_1 = m/6\pi\eta ak$. In Fletcher's experiments with oil droplets suspended in air, t_1 varies for different drops between $1 \cdot 41 \times 10^{-6}$ seconds and $3 \cdot 76 \times 10^{-6}$ seconds. For the particles employed in the present research t_1 is about 8×10^{-8} seconds.

3. Perrin, Fletcher and Eyring have used their work on Brownian movement as a basis for calculating Avogadro's number, the number of molecules in a gram-molecule. While Perrin's results, for liquid suspensions, centre about the value $6 \cdot 8 \times 10^{23}$, Fletcher and Eyring, using gases, both approximately confirm the value $6 \cdot 06 \times 10^{23}$ found by Millikan in his classic determinations of the electronic charge.

The discrepancy between these values is considerable, and raises the question of the exactitude of the equation for the movement as applied to liquids. Perrin's values of N, though differing a fair amount among themselves, yet all lie above $6 \cdot 5 \times 10^{23}$. We cannot look to failure of the law of Stokes for an explanation, for all experiments, including Perrin's own in finding the diameters of his particles, show that it holds with a high degree of accuracy for particles of the sizes used, when moving in liquids.

A possible source of error might appear to lie in some effect of the electric charges of the particles, which are of the nature of a "double layer" of the kind first treated by Helmholtz. As is well known, an electric field applied to a suspension causes the phenomenon of Cataphoresis, the drifting of the particles along the lines of force of the field, in one direction or the other according to the sign of their electric charge. Conversely, the movement of particles carrying charges sets up a potential difference in the suspending

* Millikan, 'Phys. Rev.,' 2nd Ser., vol. 21, p. 217 (1923), finds that k is $[1 + L/a \cdot (0 \cdot 864 + 0 \cdot 29e^{-1 \cdot 25a/L})]^{-1}$ in the case of air, where L is the mean free path of an air molecule.

fluid, as, *e.g.*, in Dorn's experiments*, in which sand grains and glass beads falling under gravity through a cylinder of water caused the potential in the latter to become higher at the top than at the bottom.

Now if forces of this type are called into play they may influence the motion of a particle. We can estimate this influence by extending the theory of Dorn's observations as given by Lamb†. Lamb obtains a stream function ψ of the form $(A/r+Br-\frac{1}{2}Vr^2)\sin^2\theta$, in which r, θ are the polar co-ordinates of any point in the liquid, the origin being the centre of the particle considered, whose radius is R, and which is moving in the direction $\theta = 0$, with speed V. $A = -R^3V\Big/4\left(1+\frac{3l}{R}\right)$, and $B = 3RV\left(1+\frac{2l}{R}\right)\Big/4\left(1+\frac{3l}{R}\right)$, where l is the ratio of the viscosity η to the coefficient of sliding friction β of the liquid over the particle; *i.e.*, l is a slip-coefficient of the dimension of a length. It follows that the relative velocity of the fluid and the particle at a point defined by R, θ is

$$\Theta = (A/R^3 - B/R + V)\sin\theta.$$

As a result of slip the zone on the surface of the particle bounded by θ and $\theta+d\theta$ gains electric charge at a rate $d/d\theta(2\pi R\rho\Theta\sin\theta)\,d\theta$ where ρ = surface density of charge. Regarding ρ as constant and substituting the values of A and B, Lamb deduces the rate of loss of charge per unit area, *i.e.*, the strength of the surface source, as

$$-\frac{3Vl\rho\cos\theta}{R^2}.$$

This indicates a potential ϕ at a point r, θ in the liquid such that $\phi = -\frac{3\sigma VRl\rho}{2r^2}\cos\theta+$constant, the constant, of course, being the potential at a great distance from the particle. σ is the specific resistance of the liquid.

Now, if the surface of the particle remains equipotential it follows either that the potential gradient through the double layer varies with θ, if the surface density of charge of the layer remains the same all round the particle, or, if the potential of each point of the surface of the particle adjusts itself to that of the adjacent point of the inner surface of the surrounding fluid, there is a redistribution of charge, so that ρ varies with θ. In either case there must arise a retarding force acting on the particle due to electrical charges,

* 'Wiedemann's Ann.,' vol. 10, p. 46, sec. 24 (1880).

† B.A. Report, p. 495 (1887); 'Phil. Mag.,' vol. 25, p. 52 (1888).

over and above the ordinary viscous resistance to its motion.* The order of magnitude of this force will be the same on either hypothesis. It clearly acts in the line of motion, and on the supposition of uniform surface potential is given by

$$\int_0^\pi \frac{3\sigma V l \rho}{2Rd} \cos^2 \theta \rho 2\pi R^2 \sin \theta \, d\theta,$$

where d is the thickness of the double layer. Performing the integration we find that the force is

$$-\frac{\pi\rho^2\sigma V l R}{d} = -\frac{\pi\rho^2\sigma V R\eta}{\beta d}.$$

Writing this in the form $-6\pi\eta V R \frac{\rho^2\sigma}{6\beta d}$, we see that the force is equivalent to an addition to the viscosity, such that the total effective viscosity is given by $\eta\left(1 + \frac{\rho^2\sigma}{6\beta d}\right)$. The effect of the added term is uncertain, because of the uncertainty of the values of ρ, β (or l) and d.

The thickness of the double layer is probably of the order of molecular diameter, say 3×10^{-8} cms. We may perhaps get some estimate of ρ by the aid of the equation $\rho = K\epsilon/4\pi d$, where ϵ is the potential difference associated with the double layer, and K is a dielectric coefficient, which we may dubiously assume to be that of the medium, say 80, in the case of water. From the experiments of Burton and others on the electrical properties of colloids, ϵ is of the order of $0\cdot05$ volt.

The estimation of l (or β) is more difficult. As Lamb remarks, l may well be large compared with molecular dimensions without affecting the conclusions drawn from the apparent lack of slip in such cases as the flow of liquids through capillary tubes. In this latter case consideration of slip adds to the term r^4/η of Poiseuille's law a second term $4r^3/\beta$ (r = radius of capillary). Thus all that is necessary is that $4/\beta$ must be small compared with r/η, *i.e.*, that the slip coefficient l must be small in comparison with $r/4$. Even if we make the extreme assumption that experiments show that l is less than one ten-thousandth part of r, this permits l to be as large as 10^{-6} cms. There is no evidence to show that it may not be very much less than this figure. It is doubtful if there is any real information we can draw as to its lower limits.

* It may be pointed out that this retarding force occurs in any case of movement of a charged particle in a fluid medium, not merely in that of its Brownian movements. In the flow of suspensoids it will have little effect, because of the "diluteness" of such sols, but may it not be an important factor in the great viscosity of emulsions ?

In the paper quoted Lamb makes use of the quantity $\epsilon l/d$, which replaces the ϵ of Helmholtz's original theory of Electro-Osmosis. If we take Helmholtz's figure of 1·77 times the E.M.F. of a Daniell cell, or say 2 volts for this quantity, and combine it with the values for ϵ and d suggested above, we find l is $1 \cdot 2 \times 10^{-6}$ cm., but the measurements of ϵ and of $\epsilon l/d$ refer to such different conditions of the double layer that very little weight attaches to such an estimate. If, however, we, for the moment, take l to be 10^{-6} cms., $\eta = 0 \cdot 01$ gm. cm.$^{-1}$ sec.$^{-1}$, we have the value of 10^4 for β, and substitution in the expression $\rho^2\sigma/6\beta d$ of the values above estimated and of 10^6 ohm cm. for σ, we obtain the large number $7 \cdot 7 \times 10^5$, an impossible value for a "correction." The least trustworthy of several doubtful data, as has been pointed out, is β; if we regard it as unknown the correcting term $\rho^2\sigma/6\beta d$ becomes $7 \cdot 7 \times 10^9/\beta$.

These figures show that we cannot dismiss the electrical quasi-viscous term as certainly negligible. It is of interest to calculate the value of the correction and of β, assuming that the difference between Perrin's mean value for N and the value $6 \cdot 06 \times 10^{23}$ is due to this cause. If we regard Perrin's measurements of the radii of his particles as correct, the whole difference depends on the term η, the viscosity; if, on the other hand, we consider the determination of the radii as made from their rate of fall under gravity, according to the law of Stokes, this measurement is affected by the same error in the viscosity. As the quantity measured in this way is the square of the radius, the latter quantity itself is only affected by one-half the correction to be applied to the viscosity. Thus, a 3 per cent. error is due, on the first view, to the same error in the viscosity, on the second to a 2 per cent. error.* The discrepancy between 6·5 and 6·06 is about 8 per cent., so $\rho^2\sigma/6\beta d$ must be about 0·08. This requires that β should be about 10^{11} and l about 10^{-13} cm.

4. Having in mind the above uncertainties, it seemed desirable to undertake a new measurement of N, using Perrin's method, and retaining water as the suspending medium, but using particles of a different nature from the resinous ones which he employed.

The spores of certain bacteria, such as Bacillus Anthracis, and cocci such as Staphylococcus Pyogenes, are practically perfect spheres; though any

* It must be noticed, however, that Perrin's determinations of the radius of a particle by direct measurement agreed perfectly with those made by observing the rate of fall under gravity and assuming the applicability of the law of Stokes with the usual value of the viscosity. On the above view there should have been differences of about 2½ per cent., or in the experiments giving $6 \cdot 8 \times 10^{23}$ of nearly 5 per cent.

one type may differ somewhat in size in different strains, yet a given culture contains spores or cocci of singularly equal magnitude. As, during the life of these organisms there must be passage of water through the cell walls, it appears certain that they are "wetted" by water, and that β should thus be very large (or l vanishing small), so that the electric quasi-viscous correction should be avoided.

I accordingly, in 1914, began to make measurements with the spores of B. Anthracis, but these experiments were interrupted by the outbreak of war. Except for very short periods in 1916 and 1917 I was unable to resume the work until last spring. The preliminary measurements gave a value for N of about $6 \cdot 3 \times 10^{-23}$, but little weight can be attached to this, as it depends on too few observations, and in particular the measurement of diameters was somewhat "rushed."

On taking up the work again I used Staphylococcus, partly because the very freely sporing strain of Anthrax which was first used had, unfortunately, died out, but more because it seemed undesirable to import Anthrax bacilli into a physical laboratory where other experimenters were at work and where there were no special facilities for prompt sterilization in case of accident.

The first experiments last year were with Staphylococcus aureus, later and this year with Staphylococcus albus. This last series is much the more extensive and accurate; various precautions and checks suggested by the earlier work were made use of, and all readings which showed even the slightest doubtful features were entirely discarded.

5. *General Precautions and Checks.*—As stated, the cocci of a given culture are very even in size, so that the differential centrifuging by which Perrin sorted his particles became unnecessary. At the same time, cocci frequently occur in pairs or small groups, and it is hardly necessary to say that such pairs were never used in measurement. Individuals which appear much smaller than the ordinary population occasionally occur and these also were avoided, as were any which seemed in any way damaged or abnormal. Apart from this the cocci used were in no way "selected"; that is to say, the motion of one which appeared somewhere about the middle of the eyepiece micrometer scale was observed, and when a new individual was required the stage was moved slightly and a coccus near the middle of the scale in the new field was observed in turn. In this way one avoided making any unconscious choice of particular cocci because they happened to be in especially sharp focus, or because they caught one's eye at the first glance by being momentarily stationary or by moving especially rapidly. Thus, as far as possible, the individuals

measured were a fair random sample of the population. No measurements were made very near the top or bottom of the cell containing the preparation, so that any possible disturbing effects of the walls were avoided.

The motion in a specified direction, viz., that parallel to the length of the eyepiece scale, was measured by noting positions at definite instants, signalled aurally, sometimes by a special tapping arrangement attached to a clock, marking half-minutes, later by counting half-second ticks of a chronometer. The clock rates were checked in both cases. In the earlier experiments the intervals adopted were $\frac{1}{2}$ minute, 1 minute, $1\frac{1}{2}$ minute and 2 minutes. Series of readings with these different intervals were used to verify the relation that the mean square of the displacement is proportional to the time.

In later experiments, with greater skill and generally improved technique, and with higher magnification and a better eyepiece scale, it was found possible to use shorter time-intervals, and 5, 10, 15 and 20 second intervals were adopted. This had the advantage that many more measurements could be made on each individual, while nothing was lost in accuracy, in the ease of changing the field of view, depth at which observations were made, etc. The comparison scale and the eyepiece scales and micrometer were independently measured, so that an extra check was provided on the measurement of the magnification. This measure was made in the first place in the usual way, by measuring with the eyepiece scale and micrometer a scale placed on the stage, employing precisely the same objective, eyepiece, tube-length and illumination as during the measuring of the Brownian movements. The stage scale was sometimes a scale on glass of the ordinary type, and sometimes a small transparent diffraction grating of 500 lines per centimetre.

The Thoma-Zeiss hæmocytometer cell used, as described later, in measuring the diameters of the cocci, was similarly measured by the eyepiece micrometer and independently by a travelling microscope.

6. *Measurement of Diameters of Spores or Cocci.*—Direct measurement was the only method employed in calculations, as methods depending on speed of fall require a knowledge of the density of the particles. The density was, as a matter of fact, determined in earlier experiments by floating the spores or cocci in dense solutions, but accurate values cannot be obtained in this way, as the high osmotic pressure of such solutions results in alteration or even damage of the organisms. Hence observations have to be taken at once, and only comparatively rough estimates were possible.

The direct methods were to obtain rows of stationary spores or cocci in contact with each other and to measure the lengths of these rows, either with

the eyepiece micrometer or by finding how many occupied a known length on the hæmocytometer slide. The particles were sometimes got into the immobile state by using dense suspensions and a slightly greased glass bottom to the cell, finally removing the excess of particles remaining in suspension after standing for some time. At other times I employed the method adopted by Perrin in corresponding measurements, making the suspension very slightly acid; the spores or cocci then rapidly attach themselves to the glass walls, and particularly along the scratched lines of the hæmocytometer chamber. In this way, using dense suspensions, it was easy to get long continuous lines of spheres stretching for distances of several squares of the chamber; each square is of 0·05 mm. side. It was thought that prolonged immersion in the water used in the experiments might cause changes in diameter due to osmosis, and that even such traces of acid as were used in the last-mentioned method might similarly cause errors, but observations made immediately after deposition and after standing, by both methods, showed no measurable change. Acid considerably stronger than that used in the measurements, though still dilute, produced no effect on size for some time, though it caused rapid agglutination of the greater number of the organisms.

7. *Checks on Freedom of Motion from Disturbance, etc.*—The magnitude of the Brownian movement of a particle has a very large temperature coefficient because of the factor T in the numerator of the expression for $\overline{l^2}$, and still more because of the occurrence of η in the denominator. It is therefore necessary to secure steady temperature conditions throughout a series of readings. In some of the sets of observations the suspension was therefore mounted in a small jacketing chamber, but this precaution was found unnecessary so long as sufficient time was given after the preparation was mounted and the observer had taken up his position; the temperature of the cell then remained sensibly constant for considerable periods and any set of readings which showed variations of as much as half a degree were rejected.

The routine of an experiment was thus as follows: a dense suspension of washed cocci or spores was made up and used as a stock suspension. From it was made the very dilute suspension employed in the observations, and a sample of this was placed in the observation cell; the observed drop was in contact above with the glass of the coverslip, below with that of the slide. around its edges with air. The coverslip was supported above the slide by a ring of convenient thickness, and the cell was made airtight by a little vaseline on this ring. The suspension was at once examined to see that it was of about the right density of population for convenience in measurement,

and was then left for a sufficient time to reach a steady state of temperature and distribution of particles before any readings were attempted. Very occasionally, even with these precautions, slow drifts were observed in parts of the drop, and in these cases the readings were, of course, rejected. To guard against errors of this kind from possible drifts which were too slow to be directly seen or detected on inspection of the readings, use was made of the fact that the mean square value of the displacement should bear to the square of the mean displacement the ratio $\pi : 2$. The actual ratio was calculated, and any considerable departure from the above value was regarded as evidence that the displacements were not entirely random, *i.e.*, that some motion other than the Brownian movement had occurred. The observations concerned were then again examined and usually some particular set of readings was found to be the source of trouble and was discarded. If the cause could not be "localized" in this way the whole series was rejected. A confirmatory check is the fact that the mean square of the displacement is proportional to the time. In the observations used this is found to hold very closely as is shown below, whereas in different sets in groups which were rejected on the grounds just mentioned the proportionality no longer held.

It is believed therefore that the data from which were made the calculations which follow are dependent on the Brownian movement alone, and that errors arising from temperature inequalities or from currents due to any creeping under the forces of surface tension, or to escape from the drop of microscopic air bubbles, have been avoided. The number of observations made ensures the "sampling" being adequate, and this is borne out by the close agreement of separate series made at the same temperature on different occasions, and by that between the values of Avogadro's number computed from observations at different temperatures. Any systematic error which remains would appear to be one which affects the distribution of displacements in exactly the same way as does Brownian movement itself, and this seems very improbable indeed.

The percentage accuracy attainable in such a statistical investigation as this depends almost entirely on freedom from systematic error and upon the number of observations made. The accuracy of a single measurement of a displacement is necessarily not great, even with practice in observing the movements and the best conditions of illumination and measuring apparatus: it is the large number of readings which determines the trustworthiness of the result. So far as the checks I have described and the comparison of results from different large series of readings can test the point, I am satisfied

that the necessary conditions have been secured, and that the final value given for N from the Staphylococcus albus observations is accurate to within 2 per cent.

8. The reduction of the results is simple though tedious. The observed position readings of a particle during the course of its erratic path, as read on the eyepiece scale, make up the first column of a table. The differences between successive figures of this column, marked + or — according as the motion was to the right or left, gives the second column; the entries in this are the "x"-es, the displacements in successive time-intervals of the duration selected, ½-minute, 5-second or other. The mean value of the figures of this column, irrespective of sign, is the $\bar{x}$ of equation (*b*) for the particular set of readings. Column 3 contains the squares of the corresponding displacements of column 2, and the mean for this column is the $\overline{x^2}$ of equation (*a*). Comparison of the two means gives the criterion stated above for the acceptance or rejection of the data; it was necessary to throw out very few sets of readings once the necessary preliminary precautions had been fully understood. Similar tables for other time-intervals gave the second check described in the last section. The results of such tabulations are appended for two sample sets.

Summary I.—Different time-intervals. Temperature 24° C.

(*a*) Interval 30 seconds 224 displacements $\overline{x^2} = 13 \cdot 78$.

(*b*) Interval 60 seconds 160 displacements $\overline{x^2} = 27 \cdot 81 = 2 \times 13 \cdot 90$

(*c*) Interval 90 seconds 137 displacements $\overline{x^2} = 42 \cdot 03 = 3 \times 14 \cdot 01$.

(*d*) Interval 120 seconds 106 displacements $\overline{x^2} = 55 \cdot 14 = 4 \times 13 \cdot 78$.

(Displacements are in arbitrary units, viz., those given by the eyepiece scale.)

Summary II.—Temperature 17·2° C. Set of 165 measurements.

Mean value of x, *i.e.*, $\bar{x}$, $= 3 \cdot 69$ $\qquad (\bar{x})^2 \div 2 = 6 \cdot 80$.

Mean value of x^2, *i.e.* $\overline{x^2}$, $= 21 \cdot 17$ $\qquad \overline{x^2} \div \pi = 6 \cdot 74$.

The mass of data which was compiled in this way was then sorted according to temperature, all sets lying within a range of half a degree Centigrade being grouped together to give the final data for a determination of N, the values of T and the viscosity being taken for the mean temperature of the range.

Determinations of the radius of the cocci made at intervals during the various sets of measurements showed no variations which largely exceeded those of experimental error, so a mean value of the radius was taken from all the measurements of each of the two species. By what of course is no more

than a curious coincidence, the mean value for Staph. aureus agreed exactly with that for Staph. albus.

9. The tabulations thus made are obviously bulky, but the resulting data for the final calculation of N can be very briefly stated; they fall into three groups for each variety of coccus.

Staphylococcus Aureus.

Radius of a coccus, $0 \cdot 563 \mu$. Time unit, 30 seconds.

Reduction factor to convert column 4 to cm.^{2} sec.$^{-1}$, $5 \cdot 917 \times 10^{-10}$.

Temp. ° C.	Time units (t)	No. of Observations.	$\overline{x^2}/t$	$N \times 10^{-23}$.
22·0	1	138	12·95	6·31
	4	53	12·85	
24·0	1	224	13·78	6·20
	2	160	13·90	
	3	137	14·01	
	4	106	13·78	
26·5	1	88	15·07	6·16
	4	53	14·72	

Staphylococcus Albus.

Radius of a coccus, $0 \cdot 563 \mu$. Time unit, 5 seconds.

Reduction factor to convert column 3 to cm.^{2} sec.$^{-1}$, $4 \cdot 223$ 10^{-10}.

Temp. ° C.	No. of Observations.	$\overline{x^2}/t$ (weighted mean)	$N \times 10^{-23}$.
16·2	3320	15·99	6·07
16·6	1754	16·15	6·07
17·7	1477	16·73	6·10

The weighted mean of the measurements with Staphylococcus aureus is thus $6 \cdot 22 \times 10^{23}$, that from Staphylococcus albus $6 \cdot 08 \times 10^{23}$. The error due to the directly measured quantities, the radius of the particles and the reduction factor is, I think, much less than 1 per cent., but that in the viscosity, due to inexact knowledge of the mean temperature, probably lies about that figure. I have given reasons for supposing that no systematic error has crept into the measurements of displacements, so the accuracy of the final result depends only on the errors above and on the adequacy of bulk of the data of displacements.

I think that the number of readings taken with Staphylococcus albus is ample for the application of the statistical theory on which the equation of Brownian movement depends, and that the figure deduced for Avogadro's number, viz., $6 \cdot 08 \times 10^{23}$, is therefore accurate to 1 or 2 per cent.

10. *Summary and Conclusion.*—A determination of Avogadro's number by the method of measuring the displacements, due to their Brownian movements, of small spheres suspended in water was carried out with cocci. Their surfaces may fairly be supposed to be "wetted" so that there is no slip between the water immediately adjacent and the spheres themselves, and the resistance which might arise from electrical sources depending on slip is avoided. Precautions were taken that no movements other than Brownian should be recorded. The value of N thus found, from the large number of observations made on Staphylococcus albus, is $6 \cdot 08 \times 10^{23}$.

I am indebted to the Medical Research Committee for a grant in aid of the above research. My thanks are also due to Prof. E. Emrys Roberts, of the Department of Pathology, for the cultures employed.

A Note on "The Significance of the Electrode Potential."

By J. A. V. Butler, M.Sc., University College of Swansea.

(Communicated by Prof. J. W. McBain, F.R.S.—Received July 31, 1923.)

In a recent paper* bearing the above title, Dr. Heyrovský attempts to elucidate the factors determining electrode potentials by means of a thermodynamical argument based on a cyclic process involving the following steps :—

(1) One gramme molecule of the metal vapour is withdrawn at the vapour pressure of the metal and ionized into metal ions and electrons.

(2) One gramme molecule of water vapour is ionised into $H^{\cdot}$ and OH' ions.

(3) The Me^{+} ions are allowed to combine with the OH' ions to form $MeOH$.

(4) The $MeOH$ formed and the $H^{\cdot}$ are transferred into the solution and the electrons remaining in stage (1) are condensed into platinum and returned to the metal.

(5) The $MeOH$ dissociates in solution into Me^{+} and OH' ions (hydrated)

* 'Roy. Soc. Proc.,' A, vol. 102, p. 628 (1923).

and the metal ions are transferred to the metal against the electrode potential π, thus completing the cycle.

The work terms involved in this isothermal cycle are summed and equated to zero and an expression for the electrode potential π is thus obtained.

Now, according to the second law of thermodynamics the work done in going round an isothermal cycle is zero, only provided that every stage of the process has been carried out in a perfectly reversible manner and the maximum work (or free energy) so obtained. An examination of Heyrovský's cycle reveals the fact that several stages involve irreversible processes and that free energy and total energy terms are used quite indiscriminately.

For example, in stage (1) the author remarks "Now ionize the metallic vapour, for which process an expenditure of work equal to RT+I.F is necessary, where I denotes the ionization potential . . ."

Now I.F is the total energy of ionization; that it does not correspond to the free energy of the process may be made clear from the following considerations. I.F is the work expended per gramme atom in removing an electron from each metal atom (in the metal vapour) to an infinite distance. This could be taken as the free energy of the process only if the electron could be made to yield by some means an equal amount of mechanical work in falling back into the metal ions. The dissipation of energy in heat and light in the return of the electrons appears to be inevitable, unless the movements of individual electrons could be controlled by means of a Maxwell demon. The same criticism applies to stages (2) and (3) in both of which total energy terms analogous to the work of ionization are employed.

In stage (4) the energies of hydration of MeOH and of $H^{\cdot}$ are given for the work involved in transferring these substances from the vapour phase into the solution. In order to carry out such a transfer reversibly the substance must first be expanded from its pressure (say p) to the equilibrium pressure p_1 in the vapour phase above the solution. It may now be compressed into the solution at the equilibrium pressure and the total work obtained in the transfer is RT $\log_e p/p_1$ —RT per gramme molecule.

A cyclic process such as is attempted by the author may be carried out reversibly by the use of three Van't Hoff "equilibrium boxes," all at the temperature T and containing respectively:—

1. Me, $Me^{\cdot}$ and electrons ϵ at their equilibrium pressure according to the equilibrium constant

$$K_{Me} = Me_e^{+} \cdot \varepsilon_e / Me_e$$

II. Me^{+}, OH' and MeOH at their equilibrium pressures according to

$$K_{MeOH} = Me^{+}_{e'} \cdot OH'_{e'}/MeOH_{e'}$$

III. H^2O, $H^{\cdot}$, OH' at equilibrium according to

$$K_{H_2O} = H^{\cdot}_{e} \cdot OH'_{e}/H_2O_{e}.$$

The process is carried out as follows: the maximum work obtained in the various stages being placed for brevity in brackets :—

(1) One gramme molecule of the metal vapour is withdrawn at the vapour pressure p(+RT) and expanded to the equilibrium pressure Me_e.

$$(+ RT \log_e p/Me_e).$$

(2) The metal vapour is introduced into equilibrium box I (—RT) and simultaneously one gramme molecule each of Me^{+} and of ε are withdrawn at the equilibrium pressures Me_e^{+}, ϵ_e. (+2 RT).

(3) The metal ion is expanded to its equilibrium pressure in box II (+RT $\log_e Me^{+}_e/Me^{+}_{e'}$) and introduced therein (—RT). The electrons are expanded to the pressure ϵ_M in equilibrium with the metal in the vapour space above the solution, and compressed at this pressure into the metal (+RT $\log_e \varepsilon_e/\varepsilon_M$ — RT). In addition, if ϕ_M be the potential difference at the surface of the metal an amount of electrical work $\phi_M \cdot F$ is done.

(4) One gramme molecule of water vapour is withdrawn from the solution at its vapour pressure P and expanded to the equilibrium pressure H_2O_e in box III and introduced into the latter.

$$(RT + RT \log_e P/H_2O_e - RT)$$

(5) Simultaneously 1 gramme molecule each of $H^{\cdot}$ and OH' are withdrawn from III (+2 RT) ; the OH' is expanded to its equilibrium pressure in II, $OH'_{e'}$ and introduced (RT $\log_e OH_e/OH'_{e'}$ — RT).

(6) 1 gramme molecule MeOH is withdrawn from II at $MeOH_{e'}$ and expanded to $MeOH_s$ its equilibrium pressure in the vapour phase above the solution and compressed into the latter (RT+RT $\log_e MeOH_{e'}/MeOH_s$ — RT).

(7) The gramme molecule of $H^{\cdot}$ withdrawn from III in (5) is expanded to $H^{\cdot}_s$ its equilibrium pressure in the vapour phase above the solution and compressed into the solution (RT $\log_e H^{\cdot}_e/H^{\cdot}_s$ —RT).

There may exist a potential difference E_s between the solution and its vapour against which electrical work equal to E_sF would be done (—E_sF).

(8) Finally, 1 gramme molecule of Me^{+} is deposited on the metal against the electrode potential π ; (electrical work — πF).

Summing the mechanical and electrical work terms for the whole cycle and equating to zero, we find :—

$$\pi \cdot F + E_s F - \phi_M F = RT \log_e K_{Me} - RT \log_e K_{MeOH}$$
$$+ RT \log_e K_{H_2O} - RT \log_e pP/\epsilon_M \cdot H_s \cdot MeOH_s \quad (1)$$

Now the quantities p, P, ϵ_M, H_s, $MeOH_s$ are the equilibrium pressures of the corresponding substances in the vapour phase above the liquid in the presence of the solid metal. They must therefore be in equilibrium with each other. Substituting the three equilibrium constants we find

$$RT \log_e pP \cdot /\epsilon_M \cdot H_s \cdot MeOH_s = -RT \log_e K_{Me} + RT \log_e K_{MeOH}$$
$$- RT \log_e K_{H_2O}.$$

That is, the sum of the terms on the right-hand side of equation (1) is equal to nothing, consequently the terms on the left-hand side, the algebraic sum of the differences of potential round the cycle, also sum to zero.

Actually, the cycle given by Heyrovský differs from the above in one respect, that is, instead of condensing the electrons on the metal itself he condenses them on a platinum plate and transfers them to the metal Me, thereby introducing a Peltier contact effect term ϕ'. The electrical work done in the cycle is now

$$\pi F + E_s F - (\phi_{Pt} + \phi') F ;$$

but since

$$\phi_{Me} \cdot F = (\phi_{Pt} + \phi') F,$$

our conclusion is not affected.

Summary.

1. A thermodynamical argument given in Heyrovský's paper on The Significance of the Electrode Potential is examined and it is shown that certain stages of the cyclic process employed are irreversible and that the conclusions are therefore erroneous.

2. A method of conducting the cyclic process reversibly is given and it is shown that the sum of the differences of potential round the cycle is zero ; it follows that no information regarding the relations between the electrode potentials and the various chemical equilibrium constants is obtained by the use of a cyclic process of this kind.

The Magnetic Properties of some Paramagnetic Double Sulphates at Low Temperatures.

By L. C. Jackson, M.Sc., Ph.D., A.Inst.P., and H. Kamerlingh Onnes, For. Mem. R.S.*

(Received October 13, 1923.)

In a previous paper† an account was given of a series of measurements on compounds of ferrous iron, nickel and cobalt at low temperatures. One of the objects of that investigation was to determine whether the Δ in the Weiss law $\chi(T + \Delta) = C$, which is followed by these substances at not too low temperatures, is purely a function of the "magnetic dilution" of the compound, as seemed probable from earlier measurements. It was shown that the problem is not so simple as it was thought to be at first, the run of the Δ's in general not corresponding exactly to that of the dilutions in the series of compounds—anhydrous sulphate, hydrated sulphate and ammonium double sulphate. Another point of interest was the relatively large value of Δ (= 22) in the case of cobalt ammonium sulphate, notwithstanding the great magnetic dilution of this substance.

The investigation has now been extended by the measurement of the susceptibilities of the following substances: Cobalt potassium sulphate, cobalt rubidium sulphate and manganese ammonium sulphate. These compounds were investigated with the following objects in view. The former two substances, together with cobalt ammonium sulphate, form a series of isomorphous compounds which differ from one another only in the monovalent ion in the diamagnetic part of the molecule and in the actual dimensions of the unit cells of their structures. They would thus seem to be very suitable to employ in an endeavour to determine whether in a series of compounds of exactly similar constitution, in which only the relative dimensions of the unit cells vary from member to member, the Δ is definitely a function of the mean distance apart of the paramagnetic atoms in the crystal, *i.e.*, of the dilution of the substance. Furthermore, since cobalt ammonium sulphate and cobalt rubidium sulphate are almost exactly isostructural, it would be expected that the Δ's for the two compounds would be nearly equal unless the diamagnetic

* Communication No. 168*b* from the Physical Laboratory of the University of Leiden: 'Magnetic Researches,' xxv.

† To be published shortly in the 'Phil. Trans.'

part of the molecule exerts an influence on the paramagnetic atom other than that of a mere diluent.

It would also be expected that the measurement of such a series of substances would enable one to determine whether or not the diamagnetic part of the molecule acts only as a diluent, the cobalt compounds being more suitable for this purpose than the corresponding nickel or ferrous iron compounds on account of the greater values of their Δ's.

Further, in considering the number of magnetons present in the substances it might be expected that in such a series of compounds as those at present under consideration the magneton number would be the same for all the members of the series, unless some disturbing factor due to the previous history and mode of preparation of the specimens occurs, such as found by Cabrera, Trumpler, Chatillon and Foëx. It will be seen later that the magneton numbers found for these compounds are not all equal, but become systematically greater as the molecular weight of the compound increases, in a manner which is, in all probability, not due to the mode of preparation of the specimens.

The manganese ammonium sulphate was investigated so that the properties of the manganese sulphates (anhydrous, hydrated and the ammonium double salt) might be compared with one another and with the corresponding iron, nickel and cobalt compounds. The properties of the anhydrous and the tetrahydrated manganese sulphates are already well known.*

The results of the present measurements will be found in the tables given below.

Cobalt Potassium Sulphate, $CoSO_4 . K_2SO_4 . 6H_2O$.

T.	$\chi \times 10^6$.	χ_m.	χ'_m.	$1/\chi'_m$.	$\chi'_m\,(T + 21)$.
° K.					
291·0	$23 \cdot 3_7$	$0 \cdot 0102_2$	$0 \cdot 0103_5$	$96 \cdot 6_2$	$3 \cdot 22_9$
289·5	$23 \cdot 6_5$	$0 \cdot 0103_1$	$0 \cdot 0104_7$	$95 \cdot 5_1$	$3 \cdot 25_1$
169·3	$38 \cdot 7_0$	$0 \cdot 0169_3$	$0 \cdot 0170_6$	$58 \cdot 6_2$	$3 \cdot 24_7$
77·37	$75 \cdot 0_9$	$0 \cdot 0328_4$	$0 \cdot 0329_7$	$30 \cdot 3_3$	$3 \cdot 24_3$
65·05	$84 \cdot 1_6$	$0 \cdot 0368_2$	$0 \cdot 0369_5$	$27 \cdot 0_6$	$3 \cdot 17_9$
20·42	$243 \cdot_5$	$0 \cdot 104_1$	$0 \cdot 104_2$	$9 \cdot 59_7$	$4 \cdot 31_6$
17·1	$280 \cdot_8$	$0 \cdot 120_0$	$0 \cdot 120_1$	$8 \cdot 32_7$	$4 \cdot 57_6$
14·74	$321 \cdot_0$	$0 \cdot 137_2$	$0 \cdot 137_3$	$7 \cdot 28_3$	$4 \cdot 90_7$

Magneton number = 25·32.

(T = Absolute temperature, χ = Specific susceptibility, χ_m = Molecular susceptibility, χ'_m = Molecular susceptibility corrected for diamagnetic properties of anion, etc.)

* 'Verslag, Kon. Akad. Wet. Amsterdam,' p. 1166 (1913); 'Leiden Comm.,' No. 132e.

Cobalt Rubidium Sulphate, $CoSO_4 . Rb_2SO_4 . 6H_2O$.

T.	$\chi \times 10^6$.	χ_m.	χ_m'.	$1/\chi'_m$.	$\chi'_m (T + 24)$.
° K.					
288·0	$20·9_8$	$0·0111_2$	$0·0112_6$	$88·8_1$	$3·51_3$
287·1	$21·1_1$	$0·0111_9$	$0·0113_3$	$88·2_6$	$3·52_5$
169·45	$34·0_6$	$0·0180_6$	$0·0182_0$	$54·9_5$	$3·52_1$
77·43	$64·6_4$	$0·0342_7$	$0·0344_1$	$29·0_6$	$3·49_0$
77·4	$65·0_6$	$0·0345_0$	$0·0346_4$	$28·8_7$	$3·51_3$
20·33	$201·_0$	$0·106_6$	$0·106_7$	$9·37_2$	$4·73_0$
17·04	$235·_9$	$0·125_1$	$0·125_2$	$7·88_7$	$5·13_8$
14·66	$268·_0$	$0·142_1$	$0·142_2$	$7·03_3$	$5·49_7$

Magneton number = 26·38.

Manganese Ammonium Sulphate, $MnSO_4 . (NH_4)_2 SO_4 . 6H_2O$.

T.	$\chi \times 10^6$.	χ_m.	χ'_m.	$1/\chi'_m$.	$\chi'_m (T)$.
° K.					
289·7	$37·7_9$	$0·0147_8$	$0·0149_6$	$66·8_4$	$4·33_4$
289·2	$37·6_2$	$0·0147_2$	$0·0149_0$	$67·1_1$	$4·30_9$
169·1	$65·5_8$	$0·0256_5$	$0·0258_3$	$38·7_1$	$4·36_8$
77·36	$141·_4$	$0·0553_1$	$0·0554_9$	$18·0_1$	$4·29_3$
77·32	$140·_3$	$0·0548_8$	$0·0550_6$	$18·1_6$	$4·25_7$
20·34	$546·_9$	$0·213_9$	$0·214_1$	$4·67_1$	$4·35_5$
17·07	$644·_1$	$0·252_9$	$0·253_1$	$3·95_1$	$4·32_0$
14·54	$756·_2$	$0·295_8$	$0·296_0$	$3·38_8$	$4·30_4$

Magneton number = 29·21.

The above results are shown graphically in fig. 1, the corresponding values for cobalt ammonium sulphate having been added for comparison.

It may be noted immediately that all the members of the series of cobalt compounds follow the same type of law as regards the dependence of the susceptibility on temperature. Thus they all obey the Weiss law $\chi'_m (T + \Delta) = C$ down to about 70° K., with approximately equal values of Δ, but deviate from this law at lower temperatures in such a manner that the susceptibility at the lowest temperatures is greater than the value calculated from the Weiss law. The latter phenomenon, found first for the case of cobalt ammonium sulphate, thus receives confirmation from the present results.

It may be of interest to examine the possible alternative explanations of the approximate equality of the Δ's in the series of cobalt compounds. It may be suggested that in this case the hypothesis of the direct connection between the dilution and the Δ in a paramagnetic substance here breaks down altogether, and that the Δ is either determined by the type of the

structure of the crystals of the substance or is a property of the cobalt atom itself. Neither of these suggestions, however, commends itself for general

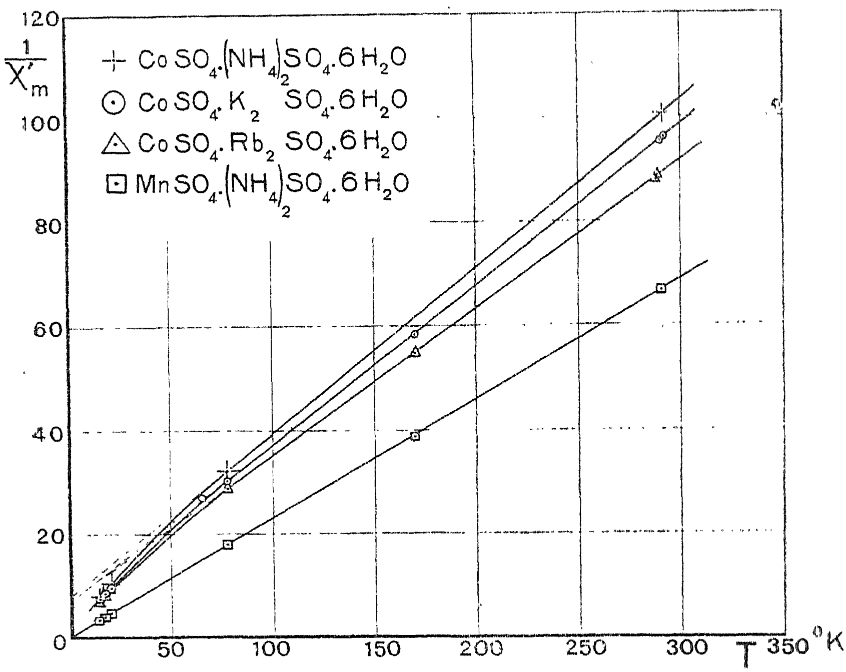


Fig. 1.

acceptance, and an explanation might more probably be found along the following lines.

Thus, it can be shown that the approximate equality of the Δ's is in agreement with the hypothesis of the direct connection of the dilution and the Δ, provided that the actual crystalline structure of the monoclinic double sulphates is taken into account. Now crystals of cobalt ammonium sulphate have been examined,* and the three principal susceptibilities and the corresponding Δ's determined. It was found that the Δ's have the following values : $\Delta_1 = 9$, $\Delta_2 = 38$, $\Delta_3 = 17$, in which the subscript 3 refers to the principal magnetic axis lying along the direction of the symmetry axis of the crystal, and the subscripts 1 and 2 to the two principal magnetic axes situated in the symmetry plane. Further, it is well known from the classic researches of Tutton that the replacement of one alkali metal by another, for example, potassium by rubidium in the monoclinic double sulphates such as those at present under consideration, changes all the dimensions of the unit cell of the crystal, but that

* Jackson, 'Diss. Leiden,' 1923 : paper shortly to be published in 'Phil. Trans.'

the change in the direction of the symmetry axis (b axis) relatively predominates. Hence since Δ_3 contributes but a moderate amount to the mean Δ (as determined by the measurements on the powdered substance) compared with Δ_2 the small changes of dimensions of the unit cell as one proceeds up the series of the double sulphates may be expected to bring about but a small change in the value of the mean Δ. A small progressive decrease of the Δ's of the powdered substances in passing up the series would thus be expected. It will be seen that of the three members of the series yet investigated cobalt potassium sulphate and cobalt ammonium sulphate arrange themselves in the correct order of decreasing Δ with increasing volume of the monovalent ion, but that cobalt rubidium sulphate which is practically isostructural with the ammonium compound has a somewhat larger value of Δ than the latter substance. This discrepancy is probably not of great significance since the accuracy of the present measurements (probable error about 1 per cent.) is not sufficiently great to show more than the fact that the Δ's of the series of substances are approximately the same. Measurements of the susceptibility with a very much greater accuracy would be required before the Δ's themselves could be determined with an accuracy approaching 1 per cent. Such measurements, especially of the principal susceptibilities of crystals, would, however, be likely to furnish information of considerable interest in connection with the crystalline structure of the substances investigated.

A further point which may be noted in connection with the cobalt compounds is that the magneton numbers are not equal but show a progressive increase as the molecular weight of the compound increases. Thus the actual values of the magneton numbers are as follows: Cobalt ammonium sulphate 24·75, cobalt potassium sulphate 25·3, cobalt rubidium sulphate 26·4, and these numbers do not approximate closely to whole numbers. This progressive increase would seem to show that the fact that the numbers are not equal is not a consequence of the mode of preparation of the specimens used. The point can, however, only be settled by investigating specimens prepared under different known conditions for each of the substances concerned.

In examining the results obtained with manganese ammonium sulphate it will be noticed that this substance follows the simple Curie law $\chi T = C$ over the whole range of temperature investigated. This behaviour may be compared with that shown by hydrated and by anhydrous manganese sulphate. The anhydrous compound follows the Weiss law with a Δ equal to 24 down to about 70° K., but shows considerable deviations from this law at lower temperatures, the susceptibility being throughout *less* than the value calculated

from the law obeyed at the higher temperatures. Hydrated manganese sulphate $MnSO_4$ $4H_2O$, on the other hand, follows Curie's law down to about 70° K., and deviates therefrom at the lower temperatures, the deviations being in the same direction as those shown by the anhydrous compound, but of smaller magnitude. The more magnetically dilute manganese ammonium sulphate, as has been seen, shows a still simpler behaviour. Thus the series of manganese sulphates may be said to show a simpler behaviour as regards the dependence of the susceptibility on temperature the greater the magnetic dilution of the substance, and thus the complications found with the corresponding ferrous iron, nickel and cobalt compounds do not occur.

A further evidence of the regularity of the behaviour of the manganese compounds is to be found in the fact that, to within the experimental error, the magneton number is the same for each of the members of the series, that of manganese ammonium sulphate being 29·2, those of both the anhydrous and the hydrated sulphate being given as 29. This is also the number found from measurements on solutions of manganese compounds.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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Norman Lockyer

SIR NORMAN LOCKYER, K.C.B., 1836–1920.

SIR NORMAN LOCKYER was the last of the remarkable body of scientific men whose observations and discoveries in the past century provided the first steps to the present marvellous developments in physical astronomy. He was still a young man when Kirchhoff founded the science of astrophysics by his epoch-making experiment on the absorption of light by luminous gases, and he was one of the few who early realised what an enormous new field of investigation was thereby opened up. While still an amateur, he rapidly achieved a foremost place among the scientific men of his time, and for more than half a century devoted himself unceasingly to inquiries in which the spectroscope played a leading part. He was a keen observer and an imaginative thinker, and never hesitated in his speculations to run directly in opposition to the current ideas of his time if thereby he could explain more to his satisfaction the new facts which he was constantly bringing to light. He was a man of strong personality, and, apart from his own direct contributions to science, he exerted a powerful personal influence for the benefit of science in many ways. He was gifted also with the power of lucid expression, and both as a lecturer and as a writer he succeeded in conveying to the lay mind a real comprehension of some of the most intricate features of the new astronomy.

Joseph Norman Lockyer was born at Rugby on May 17, 1836. He was educated in various private schools and on the Continent, and appears to have acquired a taste for scientific pursuits from his father, who founded a scientific and literary society in Rugby and took a practical interest in the development of the electric telegraph. At the age of 21 he obtained a modest appointment in the War Office, and in 1865 his marked ability secured him the office of Editor of the Army Regulations. In subsequent years he was largely instrumental in placing Army legislation upon a more satisfactory basis.

The routine of an office, however, was not enough to absorb the energies of Lockyer, and he was irresistibly drawn towards astronomy, to which he devoted most of his leisure and personal resources. He provided himself with a refracting telescope of 6¼ inches aperture, by Cooke, which remained in his possession to the end of his life. In the first instance he followed traditional lines and took up the observation of planetary surfaces. In 1862, when he was living at Wimbledon, he made careful studies of Mars during the opposition of that year, and his first scientific paper, giving an account of these observations, was communicated to the Royal Astronomical Society in 1864; it is generally acknowledged that his drawings and descriptions of the planet are among the most accurate that have ever been made.

It was as a pioneer in the application of the spectroscope to solar and stellar

problems, however, that Lockyer was destined to achieve distinction. Following the work of Kirchhoff and Bunsen, the spectra of stars and nebulæ had been studied with brilliant results by Huggins, and classifications of stars based upon extensive observations of their spectra had been prepared by Rutherford and Secchi. The sun, however, had not been studied in detail and Lockyer was practically entering a virgin field when, in 1866, he attached a small spectroscope to his 6¼-inch equatorial and observed the spectrum of a sun-spot. By thus projecting an image of the sun on the slit of the spectroscope, so that any small area could be observed independently of the rest of the solar surface, Lockyer made an advance of the first importance. It immediately gave a decisive answer to the question, then under vigorous discussion, as to the cause of the darkness of a sun-spot. The thickening of certain lines in the spot spectrum, and the absence of bright lines, proved conclusively that the darkness was due to increased absorption, as suggested by Balfour Stewart, and not to the relative feebleness of the light of interior gases seen through an opening in the photosphere, as had been suggested by Faye.

It was this same procedure that led Lockyer to his historic discovery of the method of observing the solar prominences, which had previously only been observed during total eclipses of the sun. The conditions necessary to success appear to have been clearly understood by him in 1866, when emission lines had been observed in the spectrum of Nova Coronæ. The prominences were hidden from telescopic vision by diffused sunlight near the sun's edge, but if they were masses of luminous gas, their emission lines would remain narrow and might be expected to become visible if the background of continuous spectrum arising from diffused light were sufficiently enfeebled by the use of high dispersion. In consequence of regrettable delays in the construction of a suitable instrument, for which funds had been provided by the Government Grant Committee of the Royal Society, Lockyer was unable to make a practical test of the method until October 20, 1868, when he was living at Hampstead. The bright lines were at once revealed, as he had anticipated two years before. On the same day he communicated an account of his observations to the Royal Society, announcing the existence of three bright lines, one "absolutely coincident with C," another "nearly coincident with F," and the third "near D." The observation was also communicated to the Paris Academy of Sciences, and by a remarkable coincidence, a similar communication was received on the same day from the distinguished French astronomer Janssen. Janssen had observed the total eclipse of August 18, 1868, in India, and had been so impressed by the brilliance of the prominence lines that he was convinced that they could be seen without any eclipse at all, as proved to be the case. The French Government struck a special medal in memory of the discovery and in honour of the two astronomers.

New discoveries in connection with the prominences quickly followed. On

November 5, 1868, Lockyer was able to announce that the prominences were but local upheavals of a continuous envelope round the sun, of a fairly uniform height, to which he gave the name of the *Chromosphere*, as it was the region in which coloured effects were chiefly observed during total eclipses. Soon afterwards the peculiar behaviour of the bright F line, which had been observed to widen out near the base of the chromosphere, suggested that with the aid of laboratory experiments it might be possible to discover the physical state as well as the chemical composition of the chromosphere and prominences.

Lockyer was fortunate enough about this time to be brought into collaboration with the distinguished chemist Dr. Edward Frankland in some of his laboratory researches. Frankland generously placed a convenient laboratory at Lockyer's disposal, and together they carried on experiments intended to elucidate the solar phenomena revealed by the new method of observation. Among other investigations, it was established to the satisfaction of Lockyer that the yellow line of the prominences and chromosphere, which had been named "D_3," could not be due to hydrogen, but was to be considered as originating in a then unknown gas, to which he gave the now familiar name of *helium*. It was also proved that the widening of the F line as the photosphere was approached was to be explained by an increase of pressure. With this beginning, the close association of the laboratory and the observatory became the dominant note in Lockyer's scientific work.

From this time forward, Lockyer was an acknowledged leader in solar investigations. His subsequent history is largely bound up with his evolution from his position as an amateur to that of a professional astronomer, and with his strenuous efforts to secure that our country should take a worthy part in the development of solar physics.

In view of his organising ability and scientific eminence, Lockyer was selected in 1870 to act as Secretary of the Royal Commission on Scientific Instruction and the Advancement of Science, under the Chairmanship of the Duke of Devonshire, and continued this service until the termination of the Committee's labours in 1875. Among the recommendations of the Commission was the establishment by the State of an Observatory for solar physics, similar to those which had already been founded, or contemplated, in Italy and elsewhere. As a first step to the realisation of this project, Lockyer was transferred by the then Prime Minister, Mr. Disraeli, from the War Office to the Science and Art Department at South Kensington. Facilities were there afforded him for proceeding with his researches in such intervals as could be spared from his official duties, which included the inspection of Training Colleges and the organisation of a loan collection of scientific apparatus. The permanent collection which now constitutes the Science Museum had its beginnings in this Exhibition, and Lockyer devoted himself to its interests unsparingly and with a high ideal as to the value to the nation of carefully selected scientific exhibits. The 6¼-inch telescope was removed to South

Kensington and the observational equipment was augmented by various loans, which included a photoheliograph placed at his disposal by the Astronomer Royal. He was enabled to maintain some sort of continuity in his scientific labours by the Government Grant Committee's provision of funds for the employment of an assistant and the purchase of necessary photographic materials.

In 1879, in response to a strong recommendation by the Duke of Devonshire's Commission, backed by memorials presented by many eminent men of science, the Solar Physics Committee was appointed by the Government to advise on the methods of carrying on observations in solar physics, and Lockyer doubtless hoped that their deliberations would lead to the foundation of an Astrophysical Observatory, which might ultimately become comparable in importance with the Royal Observatory at Greenwich. The immediate result was the establishment of a temporary observatory at South Kensington, maintained by a small grant in aid, from year to year, for the provision of chemicals and apparatus and payment for assistance. During the first six years, the members of the Committee, among whom were Stokes, Balfour Stewart, Abney and Christie, took a personal share in the work of the Observatory, but from 1885 onwards the functions of the Committee became mainly consultative, and the whole of the work was initiated and directed by Lockyer.

By his appointment as Lecturer in 1881, and afterwards as Professor of Astronomical Physics in the Royal College of Science in 1887, Lockyer was enabled to devote himself more completely to his scientific work, and eventually to utilise the services of a demonstrator and of research students. Other additions to his equipment and staff were made from time to time, and on his retirement from his professorship, on reaching the age limit, in 1901, the Observatory was placed on a semi-permanent basis, with a staff of 6 assistants and Lockyer as Director.

When it became necessary to vacate the site at South Kensington, in view of the proposed erection of a new building for the Science Museum, Lockyer was full of hope that his dream of directing a permanent Astrophysical Observatory, maintained by the State, would early be realised. He made careful plans and selected a suitable site at Fosterdown, in Surrey, but on a majority recommendation of a Departmental Committee which was appointed to advise the Government on the matter, the Observatory was transferred, in 1913, to the University of Cambridge. Lockyer was intensely disappointed with this decision, but although he was then 76 years of age he resolved to start afresh. With his accustomed energy and determination he planned a new Observatory at Sidmouth, where he had recently built a house, and it was not very long before buildings and instruments were erected and active observations begun. In this project he had the generous co-operation of Lady Lockyer and others, among whom was Colonel Frank McClean, who also presented the 12-inch equatorial which had been used for work on stellar

spectra by his father, the late Mr. Frank McClean, F.R.S. Some of the instruments from South Kensington had also been placed at Lockyer's disposal, including a 10-inch refractor and a 9-inch prismatic camera. These, with an excellent library and a small laboratory, enabled the work on the photography and interpretation of stellar spectra to be continued almost without a break, and several papers on stellar classification were issued as Observatory Bulletins. The Observatory was incorporated in 1916, and since Lockyer's death has been re-named "The Norman Lockyer Observatory." It is a worthy memorial of its distinguished founder, and it may be hoped that further aid will be forthcoming to ensure its permanent maintenance.

Notwithstanding the almost continuously unsettled conditions under which he laboured, Lockyer got through an immense amount of work. "The more one has to do, the more one does," was his favourite motto. His contributions to astronomy and spectroscopy form the subject-matter of more than 200 papers, the majority of which were communicated to the Royal Society. From time to time the results of his researches were elaborated in the form of books, among which are his 'Solar Physics,' 'The Chemistry of the Sun,' 'Recent and Coming Eclipses,' 'The Meteoritic Hypothesis,' 'The Sun's Place in Nature,' and 'Inorganic Evolution.'

From the beginning Lockyer showed a tendency to generalise on a large scale, and regarded his work both in the laboratory and in the observatory as a means to a wider knowledge of the fundamental processes of Nature. He recognised at a very early stage that the spectrum of a substance depended not only on its chemical composition, but also on the physical conditions under which it was made luminous, and he conceived the possibility that in this fact lay the key to processes taking place within the atoms and molecules, which up to that time had been regarded as indivisible units. With characteristic boldness and originality of thought he put forward, in 1873, his well-known dissociation hypothesis, according to which the character of the ultimate constituents of the so-called elements depended on temperature. At a given temperature, or through a certain range of temperature, the atom of an element consisted of a certain "molecular grouping," which was characteristic of the element at that temperature, but which was by no means the indestructible unit which the chemist postulated. At a higher temperature it was liable to be broken up into simpler groupings, which might or might not be all alike. These simpler forms had not been detected by the chemist because chemical operations were carried on within a small range of temperature. In the intense heat of the electric arc and spark, and still more in that of the sun and stars, dissociation could take place, and it was in the spectra of substances under these extreme conditions, therefore, that evidence of the dissociation was to be sought.

The evidence he brought together was of a varied character, and some of that which depended on solar observations is no longer valid. On the other

hand, his laboratory and stellar investigations are even now of the first importance, and, in the light of present knowledge, there is no doubt that the idea of dissociation was as near an approach as was possible in Lockyer's time to the true explanation of the variability of spectra. By the simple device of projecting the image of a horizontal arc on a vertical slit, he showed that, whilst some lines appeared short, and therefore were produced only in the core of the arc, there were others which, because of their much greater length, must have been produced also in the outer flame. This discovery at once disposed of the earlier notion that to each element there corresponded only one spectrum, and to Lockyer's mind the simplest, and perhaps the only conceivable, explanation was that dissociation took place in the hot interior of the arc, and that the products gave rise to the short lines there produced.

In later years he reached a much fuller conception of the influence of temperature on spectra, and the idea of "enhanced lines," published in 1897, forms the experimental basis of the modern theory of successive ionisation of atoms. He showed that, on passing from the arc to the spark, certain lines are strengthened or appear as new lines in the spectrum. These are the enhanced lines, and, attributing their appearance to the influence of a higher temperature than that necessary to produce the arc lines, Lockyer was able to use their presence in stellar spectra as a criterion of stellar temperatures. He imagined a condition of temperature at present unattainable on the earth, in which only the enhanced lines would be able to survive, and in this way he was able to interpret celestial spectra which could not be reproduced in the laboratory. To the origins of the enhanced lines he gave the name "proto-elements," and he regarded them as simplified forms of the elements with which we are familiar at lower temperatures. So far he correctly anticipated the modern view, but in his ideas that the atomic weights of the proto-elements were greatly below those of the corresponding elements, and that at a sufficiently high temperature all atoms would be reduced to units yielding identical spectra, he introduced hypotheses from which modern thought has definitely departed.

The essential correctness of Lockyer's explanation of spectral variations, however, is now generally recognised, and the following passage from an article in the 'Philosophical Magazine' for December, 1922, by Dr. M. N. Saha, shows how closely he approached the modern point of view :—

"It will be seen that the above discussion mainly centres round the life-work of the late Sir Norman Lockyer. To him is due not only the idea, but also extended and elaborate studies, of the enhanced and super-enhanced lines of elements, and their application to the study of the ordered sequence in stellar spectra. In this connection, attention may be drawn to the views which he presented in his 'Inorganic Evolution.' He tried to impress the idea that the enhanced lines are due to some proto-form or fractional part of chemical atoms. But in those days the atom was an 'elastic solid sphere,' and his

ideas did not find many adherents. The real significance of his work is being realised in these days of the Rutherford-Bohr theory of atomic constitution."

Lockyer's studies of the variations of spectra, and his recognition of the significance of the enhanced lines, undoubtedly constitute one of the most important chapters in the history of astrophysics. There are abundant indications in the recent work of Saha and others that the continued investigation of such lines, especially in regard to their arrangement in series, will find a further important application in the determination of the absolute temperatures and densities of stellar atmospheres.

Far-reaching as was the idea of dissociation, an even wider generalisation was to follow. In 'The Meteoritic Hypothesis,' published in 1890, Lockyer brought together a large amount of evidence for the view that all self-luminous celestial bodies consist of, or have originated from, meteoritic swarms. The idea seems to have occurred to him as early as 1874, when, in an article in 'Nature,' he put forward an explanation of the principal phenomena of Coggia's comet, which involved collisions between small particles as the cause of the comet's luminosity. Tait had previously made a similar suggestion as a possible cause of the luminosity of both comets and nebulæ, and Lockyer conceived the possibility of extending the idea into a comprehensive scheme of celestial evolution. It was not until 1887, however, that he developed the idea and gave it a definite form.

During several years he carried out a long programme of experiments and observations which strengthened his conviction that all existing forms of cosmical bodies could be explained as the result of the action of gravitation between and within swarms of meteorites. In these days of exact measurement, some of Lockyer's crucial identifications are no longer admissible, but the conclusions at which he arrived are in some respects much more in accord with recent developments than were the contrary beliefs which then prevailed. He pictured an original swarm of meteorites, which would slowly condense under the mutual gravitation of its parts, so that collisions would become more and more frequent as condensation proceeded. Such a swarm would become a nebula, in its earliest visible form, when the temperature was high enough to render the vaporised portions of the meteorites luminous. With the progress of condensation the swarm would eventually appear merely as a luminous point, or star, though it was still a swarm of meteorites increasing in temperature on account of frequent impacts. The process of condensation and rise of temperature would continue until the whole of the swarm had become vaporised, after which the temperature would begin to fall and the star would slowly shrink and eventually cease to be luminous.

The idea of a course of evolution in which a star first rose and then fell in temperature ran directly counter to the then prevailing view, according to which cooling was a continuous process throughout the life of a star, the nebulæ themselves being supposed to be intensely hot. There was nothing, however,

in the new view which violated physical principles, for Lane and Ritter had already shown that a condensing and radiating mass of gas would at first rise in temperature, and Sir George Darwin ('Phil. Trans.' A, vol. 180, p. 1 (1889)) proved later that the laws governing the mechanical properties of gases are equally applicable to meteoritic swarms.

The meteoritic hypothesis, as originally propounded, was based mainly upon the accumulated records of other observers, but for its further development, while maintaining his solar investigations, Lockyer wisely determined to secure observations of the stars and nebulæ for himself. At South Kensington he at first employed a small 2-prism star spectroscope attached to the 10-inch Cooke equatorial, but after 1889 most of his work was carried on with prismatic cameras of 6 and 9 inches aperture. At a later stage he acquired a 36-inch reflector, having a mirror presented by his friend, Dr. A. A. Common, but the mounting of this instrument was never satisfactory and few results were obtained with it. In order to enlarge his opportunities of obtaining photographs, Lockyer built a country house at Westgate-on-Sea, and in 1889 erected a 30-inch reflector, which was utilised by himself and by an assistant from South Kensington during week-ends and vacations. The Westgate instrument was removed to South Kensington a few years later, and many valuable photographs were obtained by its use. The atmospheric conditions in South Kensington left much to be desired, but Lockyer succeeded in communicating some of his enthusiasm to his assistants, and by taking advantage of every opportunity, at whatever hour of the night, a very fine series of photographs of stellar spectra was secured.

Lockyer was thus enabled to produce extensive and valuable lists of the lines occurring in the different types of stellar spectra, and, with the aid of his laboratory experiments, was able to indicate the chemical origins of a large percentage of the lines observed. The tables thus prepared were the first of large scope which had any considerable claim to accuracy, and are still among the chief sources of information with regard to the positions and origins of stellar lines.

The evidence afforded by the new photographic data enabled Lockyer greatly to strengthen the arguments in favour of his contention that celestial evolution did not proceed solely in the direction of falling temperature. It was found, for example, when stars at any specified temperature were classed together by reference to the relative intensities of arc and enhanced lines, that there were differences which required their separation into two distinct groups. The spectra were therefore not determined entirely by temperature, and the differences were attributed to the different degrees of condensation, one representing uncondensed swarms of increasing temperature, and the other stars which were on the down-grade.

Numerous papers bearing upon stellar classification were published by Lockyer, among which one on "The Chemistry of the Hottest Stars"

('Roy. Soc. Proc.,' vol. 61, p. 148 (1897)) is especially noteworthy as an example of Lockyer's illuminating methods of presenting detail, and as giving a masterly summary of the question of classification and its bearing upon the dissociation hypothesis. After some earlier efforts, Lockyer finally proposed a new classification of stars, in which he elaborated the idea of naming the different groups from typical stars, such as, for example, "Sirian," from the type star Sirius. This system undoubtedly had a good deal to recommend it, but astronomers generally have preferred to adopt the Harvard alphabetical notation. This, however, in no way diminishes the value of Lockyer's contribution to the subject in the form of detailed descriptions of the spectra of stars of the various types.

For many years Lockyer was practically alone in recognising the existence of stars of increasing temperature, and it was a constant source of regret to him that so much work on stellar distribution, and on other matters relating to the structure of the sidereal universe, was being done without taking any account of this feature. In his declining years, however, he was greatly cheered to see that his view of the general course of stellar evolution was working its way into general acceptance, mainly through the investigations of Prof. H. N. Russell. It is true that there are important differences in detail between the evolutionary sequences formulated by Lockyer and Russell, but the same central idea is common to both. Lockyer's scheme was based upon the spectra alone, while Russell was able to utilise additional data relating to absolute magnitudes which had then been accumulated, and was thus led to his division of stars of similar spectral type into "giants" of low density and "dwarfs" having a density comparable with, or greater than, that of the sun. The helium stars and stars having the so-called "*c*" characteristic (unusually sharp lines) occupy similar places in the two systems, but for other classes of stars Lockyer's criteria did not enable him to distinguish the giants from the dwarfs. Thus, Lockyer had placed all the red stars of the M-type in a single group, representing the first stage of condensation from nebulæ, whereas the giant stars of this class only can now be so placed. The leading feature of Lockyer's classification, nevertheless, is preserved in the theory of Russell.

Lockyer naturally attached great importance to solar eclipses as providing special opportunities for investigating the constitution of the sun, and thence, to some extent, of the stars. Beginning with an eclipse in Sicily in 1870, on which occasion he was leader of a large party but was prevented by clouds from making observations, and ending with an eclipse in Majorca in 1905, he personally took part in eight expeditions, and, in addition, sent out assistants to make observations on several other occasions. The outstanding feature of his eclipse work was the introduction and use of the slitless spectroscope, first for visual observations in India in 1871, and afterwards in the form of a prismatic camera for obtaining photographic records. The first striking success with this instrument was at the eclipse in Senegambia in 1893, when

his assistant, Mr. Fowler, obtained numerous plates showing the distribution of prominence and coronal emissions at all points of the sun's limb, and some 300 bright lines originating in the lower chromosphere. New coronal lines were also then observed, and it was further clearly established that the lines of hydrogen and calcium which had previously been observed in the coronal spectrum with slit spectroscopes did not truly belong to the corona, but were due to atmospheric diffusion of the light of the chromosphere and prominences.

A more complete record of the spectrum of the lower chromosphere, or "flash spectrum," was secured in 1896 by Mr. W. Shackleton, who had been equipped with a prismatic camera, and sent out by Lockyer with Sir George Baden Powell's expedition to Novaya Zemlya. A more powerful instrument was employed in India in 1898, and photographs were obtained which revealed still greater detail of the flash spectrum, besides proving that the famous green line of the coronal spectrum (λ 5303) was not coincident with the Fraunhofer line "1474 K," as had been supposed from the time of its discovery.

An important feature of photographs taken with the prismatic camera is that vapours extending to different heights in the chromosphere are represented by arcs of different lengths, and much valuable information on this subject was obtained by Lockyer. With the aid of his laboratory researches he was further able to identify the majority of the lines of the flash spectrum, and to show the important part played by the enhanced lines of various metallic elements. He was certainly mistaken, however, in his deduction from such photographs that an important part of the Fraunhofer absorption must be produced by cooler vapours overlying the visible chromosphere.

The general phenomena of a total eclipse were not neglected by Lockyer. He had a great gift for organisation, and on many of his expeditions he was able to enlarge his programme by utilising the services of officers and men of the Royal Navy who were fortunate enough to be attached to ships which had been detailed by the Admiralty to convey the observers to their station, and to render such assistance as might be desired. Lockyer was never happier in his scientific work than on such occasions. He had unlimited confidence in the abilities and adaptability of naval men, and took a keen delight in lecturing to them and training them to take definite parts in the programme of observations to be made during the critical moments of totality. He invariably took out a number of instruments to be used in this way, and numerous observations were secured which it would otherwise have been impossible to obtain. Interesting narratives of some of these expeditions are given in his book on 'Recent and Coming Eclipses' (1897 and 1900).

Almost from the very beginning of his scientific career, Lockyer was strongly attracted by the question of the relation between the state of the sun and meteorological conditions on the earth. There was already some evidence of the recurrence of famines in India in an 11-yearly period corresponding with the periodicity of sun-spots, and a somewhat similar period had been

suspected in the recurrence of cyclones in the Indian Ocean. The probable utility of solar research in this connection was, in fact, urged in the memorial to the Government which led to the establishment of the Solar Physics Observatory, and the investigation of such relationships was regarded from the first as one of the most important of its functions.

Lockyer early recognised the need for a more continuous record of solar conditions than could possibly be obtained in England, and was instrumental in inducing the Indian Government to make arrangements for photographs of the sun to be taken daily. A very valuable supplement to the Greenwich series has thus been secured, extending from 1878 to the present time. In 1879 Lockyer commenced a systematic record of the spectra of sun-spots, and in due course announced the discovery of variations which suggested that while at sun-spot minima the most widened lines were representative of familiar elements, those most affected at maxima were lines of unknown origin, possibly representing products of dissociation due to increased temperature. His conclusion that the sun was hotter at maximum than at minimum is quite in agreement with present views, but the supposed variations of spectrum on which it was based have not been confirmed. It would appear that in his anxiety to maintain a series of comparable records as frequently as possible, making allowance for the uncertainties of weather, he unduly restricted the daily record to that of the twelve most widened lines in the region of observation in each spot, and thus gave scope for a misleading selection of lines.

In 1898, in collaboration with his son, Dr. W. J. S. Lockyer, who had then joined the staff of the Observatory, Lockyer entered upon an extensive investigation of meteorological records in relation to solar phenomena, beginning with rainfall in India. Among other results it was established that Indian pressure maxima were related to a solar prominence cycle of about 3·7 years, while the pressure maxima at Cordoba, in South America, exhibited an inverse relation, high pressures in India being accompanied by low pressures at Cordoba. The Indian pressure area was subsequently found to extend to Australia, East Indies, Mauritius, Egypt, East Africa, Europe and Canada, while the Cordoba region included not only South and Central America, but also the United States and Asiatic Russia. The discovery of this barometric "see-saw," which was corroborated by Bigelow, marked a distinct advance, and raised hopes that the possibility of long-period forecasting of weather could not be far distant.

Numerous other papers followed, but no finality could be reached on account of the difficulty of extending the comparison to the earth's atmosphere as a whole. The investigations, however, attracted the attention of meteorologists, and following a report which he presented to the International Meteorological Committee at Southport in 1903, a Solar Commission was constituted, of which Lockyer was appointed President in the following year. He was subsequently

enabled to utilise more extensive systematic data supplied by members of this Commission. The investigation is beset with difficulties, but Lockyer never lost his confidence that long-period forecasting would eventually be possible. His work undoubtedly did much to stimulate advances in meteorological work, especially in India.

One of Lockyer's chief characteristics was his versatility. While thoroughly immersed in the controversies which had arisen regarding his hypotheses of dissociation and of the meteoritic origin of the cosmic bodies, he turned his attention in a new direction. A visit to Egypt had aroused in his mind the idea that if, as seemed probable, the ancient temples there had been constructed for the worship of the heavenly bodies, it should be possible, by a study of their orientations, to determine the dates at which they were erected. Assuming that they were directed towards the more prominent heavenly bodies at rising or setting at particular times of the year, the known changes of position of the bodies due to the precession of the equinoxes would be sufficient to fix the required dates within fairly narrow limits. Lockyer brought together the results of these inquiries in a book of great interest entitled 'The Dawn of Astronomy,' which was published in 1894. Later, he made extensive investigations of British stone circles, of which he gave an account in 'Stonehenge and other British Monuments Astronomically considered' (1906 and 1909). These works attracted a great deal of attention from archæologists who had been endeavouring to settle the same problems from other data.

Among the many contributions which Lockyer made to the advancement of science in general, there is none which has had so great an influence as the inauguration of the journal 'Nature,' of which, from its establishment in 1869 until a few months before his death, he was the editor and leading spirit. Three years' experience in the sixties as scientific editor of 'The Reader'—a weekly literary and scientific organ, which came to an undeserved end in 1865 through lack of funds—gave him the necessary journalistic training for the work, and, correctly gauging the need for a periodical devoted entirely to Science, he soon afterwards founded 'Nature,' in co-operation with Mr. Alexander Macmillan. How truly his instinct led him in this matter may be judged from the fact that, from its inception to the present time, 'Nature' has preserved, not only its original aims and principles, but also the form and general arrangement with which it began its career. It was a great satisfaction to Lockyer that, in this direction at least, his efforts for the well-being of Science bore such abundant fruit.

In the more difficult task of awakening the rulers of the Empire to the importance of Science as a national asset, he was only partially successful—not, however, through lack of enthusiasm or persistent attack. Perhaps his outstanding effort in this direction was that which he made as President of the British Association at Southport in 1903, when, in an impassioned address on "The Influence of Brain-power on History," he made a strong and

urgent plea for the recognition of education in Science as one of the first duties of an enlightened Imperial administration. It was his hope that the British Association would support his appeal by making it one of the objects of the Association's existence. That hope was not realised, and undaunted as ever he set to work to establish a new body for the purpose. It was at his instigation that the British Science Guild was founded in 1905, and to the end of his life he continued to give it all the inspiration and active support that lay in his power.

Lockyer also rendered a valuable service to Science in another direction. On the decision of the Commissioners for the Exhibition of 1851 to establish scholarships, he was appointed, in 1890, with Huxley, Roscoe and Garnett, to co-operate with Lord Playfair and Mr. Mundella in drawing up a scheme for the regulation of the awards. We believe that it was mainly through Lockyer's representations that these scholarships were established on a post-graduate basis, to be awarded to students who gave high promise of capacity for scientific research. He was himself appointed a Royal Commissioner in 1894. Throughout his connection with this body he kept a jealous eye on the disposal of the remaining land under the control of the Commissioners on the South Kensington Estate, and it is largely due to his efforts that an adequate proportion has been allotted for scientific purposes.

Lockyer was very successful in his work as a professor. His lectures were always carefully prepared, and he missed no opportunity of illustrating them by lantern slides, diagrams, or working models, many of which were of his own design. He had an impressive delivery, and always held the attention of his students with ease. He laid great stress on the need for students to see and do things for themselves, and instituted a course of practical training in the use of instruments employed in nearly every department of astronomy. The special courses for teachers which were at times organised by the Board of Education, extending over three weeks during the month of July, were greatly enjoyed by Lockyer himself, and were always highly appreciated by the teachers. He certainly succeeded in awakening a genuine interest in astronomy in a multitude of students.

Many distinctions were received by Lockyer in recognition of his services to Science. He was elected a Fellow of the Royal Society in 1869, served on the Council for three periods of two years each, and was Vice-President in 1892–93. He was Rede Lecturer at Cambridge in 1871, was awarded the Rumford medal by the Royal Society in 1874, and was Bakerian Lecturer in 1874 and 1888. In 1875 he was elected a Corresponding Member of the Paris Academy of Sciences, and in the same year was awarded the Janssen Medal. He was created Companion of the Bath in 1894 and Knight Commander in 1897. The Universities of Glasgow, Edinburgh and Aberdeen conferred upon him the honorary degree of LL.D.; those of Cambridge and Sheffield the Hon. Sc.D., and that of Oxford the Hon. D.Sc. He was President

of the British Association in 1903–04. He was also elected to honorary membership of nearly all the leading scientific societies of Europe and America.

Lockyer was twice married, his first wife, who died in 1879, being the younger daughter of Mr. William James, of Trebenshon, near Abergavenny. In 1903 he married the younger daughter of Mr. S. W. Browne, of Bridgwater and Clifton, who was the widow of Mr. Bernard E. Brodhurst, F.R.C.S. Lady Lockyer, together with four sons and two daughters of the first marriage, survives him. He died at Sidmouth on August 14, 1920, and was buried in the neighbouring churchyard at Salcombe Regis. A portrait medallion, erected in the observatory by his relatives and friends, was unveiled by the Astronomer Royal on July 22, 1922.

Lockyer's mind had the restless character of those to whom every difficulty is a fresh inspiration. His enthusiasm never failed him, despite repeated disappointments and opposition. He was not easily understood. His temperament was of a peculiar character—perhaps inseparable from the exceptional qualities of his intellect—and those whose acquaintance with him was of a casual kind were apt to be misled as to his real nature. To his friends—and they were many—his companionship and the stimulating influence of his unwearied mental activity were among their most cherished possessions.

A. F.

JAMES ARTHUR POLLOCK, 1865–1922.

James Arthur Pollock was born on November 17, 1865, at Douglas, County Cork, a small village near the City of Cork, where his father, James Wheeler Pollock, had a flax-spinning and weaving mill, manufacturing damasks. The Pollocks were originally a Scotch family, which settled in the North of Ireland some generations before the subject of this memoir was born. The grandfather, Hugh Pollock, migrated from County Down and finally established himself in Cork, building a flax mill at Douglas. He seems to have been a pioneer of flax spinning and weaving in this part of Ireland, and James Wheeler Pollock inherited the mill, and in conjunction with his partner Wallis enlarged it considerably. They were fairly successful for some twenty years, but conditions became unfavourable in the eighties and the business was given up.

In 1861, James Wheeler Pollock married Emma Brierley, of Birkenhead, a member of the Rochdale family of that name. There were two sons and a daughter—the elder son, Hugh, was a year older than James Arthur—and both sons were intended for the flax mill, Hugh as a weaver and Arthur as a spinner. The writer remembers James Wheeler Pollock very well—he was the typical handsome courtly Irish gentleman of fifty years ago.

The boys, Hugh and James Arthur (usually known as Arthur), were educated at the Manchester Grammar School, and at the early age of fifteen Arthur Pollock matriculated at Queen's College, Cork, and at Trinity College, Dublin. At Cork he graduated with the degree of Bachelor of Engineering; but he never finished his course at Trinity College, for in the meantime it was decided to give up the flax mills and the family prepared to emigrate to Sydney, New South Wales. Arthur Pollock sailed for Sydney in January, 1885, and was followed by his brother a year later, and by the rest of the family in 1886.

Soon after his arrival at Sydney Pollock was appointed second Astronomical Assistant at the Sydney Observatory under the late H. C. Russell, C.M.G., F.R.S., who was the Government Astronomer. He stayed at the Observatory for upwards of two years, during which time he attended some lectures at the Sydney University, and in 1888 he was given a year's leave of absence to enable him to take a further course in Physics and Mathematics at that University, though Russell was very sorry to lose him. He was awarded the Gold Medal for Physics, and was appointed Demonstrator in that subject under Prof. R. Threlfall in 1889.

Pollock's two years' training at the Observatory had a very great and lasting influence on him. Throughout his life his instinct was rather to minimise instrumental imperfection by good observations and corrections than to throw an instrument away and make a better. He loved astronomical calculations, which satisfied his precise and logical mind in a way that speculative physics

never did. H. C. Russell, too, was a great mechanic—he was meteorologist as well as astronomer, and practically all his meteorological instruments were of his own invention and construction—and this had its influence on Pollock. For instance, years afterwards he was found "cleaning" his watch, and it appeared he was doing this because it had been considered weak at the observatory to employ a watchmaker!

At the Physical Laboratory of the University of Sydney there was great activity in the improvisation of apparatus under the direction of the late James Cook, F.R.A.S., and this enabled Pollock to extend his experience, and he finally became a past master in the construction and adjustment of apparatus rather than as a designer of new instruments.

During the eleven years 1888 to 1899 (when he succeeded to the Professorship) Pollock worked in the Laboratory literally day and night. He published a considerable number of papers in collaboration with his chief, but his critical sense and fear of cumbering the literature prevented his publishing much work of his own. For instance, he acquired extraordinary dexterity in the manipulation of the half-silvered mirrors of Michelson & Morley, and applied his skill in all sorts of optical experiments, about which he published nothing—his reason being that the results did not advance our knowledge of the subject, *i.e.*, they simply confirmed what was known; and the fact that this confirmation was obtained by new methods did not in Pollock's opinion justify any publication. His modesty and dislike of appearing in anything like a prominent position were excessive. He was for five-and-thirty years a Member of the Royal Society of New South Wales, for eleven years he was one of the Honorary Secretaries, but nothing could persuade him to accept the Presidency. He was pressed to take the position of Dean of the Faculty of Science of the University again and again. He would have none of it. He did, however, act as President of Section A of the Australian Association for the advancement of Science in 1909; probably he did not regard the Presidency of a Section as implying publicity!

The years of his Demonstratorship were possibly among the happiest of Pollock's life. Periods of enthusiastic work were relieved by short but equally strenuous holidays, generally in yachting excursions up and down the Australian coast under the guidance of the late Alexander Oliver, at first Parliamentary Draughtsman and afterwards Judge of the Land Court of New South Wales. Oliver was a scholar and a wit, an unsurpassed yachtsman and lover of the wilds. Pollock became a moderate sailor-man himself, but his cheeriness and unselfishness would have made him welcome in any party even if he had learned nothing of sailing. It may also be said that he was extremely popular with the staff and students of the University, and lived on terms of the greatest intimacy and affection with his chief, with whom he both worked and played.

From 1895 onwards Threlfall became more and more interested in technical work, especially in electrochemistry, and a suitable opportunity having arisen

in 1898, while he was on leave in England, he resigned his professorship and Pollock succeeded him, being elected early in 1899. This office he retained till his death on May 24, 1922. As a Professor, and in spite of his modest and retiring disposition, he soon became an important factor in all University affairs. His teaching was conscientious, clear and precise, and he insisted on his students acquiring similar habits of clarity and precision in their writings.

His scientific work for some years, however, was interrupted by the long illness and eventual death of his brother Hugh, to whom he was devoted. What leisure Pollock's teaching left him—and he took a severe view of his duties—was mainly spent in looking after Hugh. After Hugh's death Pollock was able to do more scientific work, and this continued till the outbreak of the War, when he was in his forty-ninth year, afforded him just such an opportunity as appealed to his chivalrous nature. It may almost be said that he experienced "a call." The opportunity, however, at first was lacking, but in November, 1915, it was decided by the Federal Defence Department to form a Military Mining Corps of two Battalions of picked miners, under the command of Sir Edgeworth David, F.R.S., Professor of Geology in the University of Sydney. Pollock immediately asked to be allowed to go with them in any capacity, but it was not till he had shown his metal by devising the "Geo-telephone" for underground listening, that he was commissioned as Captain to superintend the manufacture of these instruments and to instruct the Officers and N.C.Os. of the Australian Mining Corps in their use. Sir Edgeworth David, his comrade in arms, contributed to the Sydney University Magazine, "Hermes," August, 1922, the following fine account of Pollock's activities as a soldier :—

> "Never have I seen Professor Pollock's ever cheerful face more radiant with happiness than when the news came through that he had been appointed. To the fiery zeal of the Crusader he brought the heart of a boy, rejoicing in the great adventure that now lay before him. . . .
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> . . . . "In our camp at Casula, near Liverpool, on our troopship the 'Ulysses,' on active service on the Western Front, no officer of the Mining Corps was more respected or beloved, alike by sappers, N.C.Os. and brother officers, than was Captain Pollock. He was a perfect Mark Tapley for cheerfulness at all times and places, and had not only a rare appreciation of the humorous, but, as far as was consistent with the maintenance of good discipline, always counselled leniency in dealing with the miners' misdemeanours. . . .
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> . . . . "After our arrival at Hazebrouck the Mining Corps, soon reinforced by a second batallion, was broken up into companies, which were distributed along the Western Front, from Ypres to Givenchy-lez-la Bassée, while Captain Pollock was appointed by Sir Herbert Plumer, Commander of the Second Army, to take charge of what was called 'The Mining School,' at Proven, near Poperinghe. Here he established what

may be termed a military physics laboratory. His special work was that of studying sound waves transmitted through the earth, and instructing officers and N.C.Os. of all the numerous tunnelling companies of the Second Army Area, Canadians, Australians and men from the Old Country, in the best methods of using the new French instrument, the geophone, which had just then superseded the geo-telephone.

"These instruments had to be tried out from time to time under front-line conditions, which necessitated Captain Pollock's paying occasional visits to the tunnels of our No. 1 Australian Tunnelling Company at Hill 60, near Ypres, and the track to Hill 60, even by the Hell Fire Corner route, was no health resort in those days.

"Great anxiety was felt lest one of the frequent camouflets (heavy charges fired underground, but not sufficiently heavy to break the surface), should detonate some of our big mines, and this new problem was attacked by Captain Pollock with the help of instruments designed partly by himself, partly by C. V. Boys, F.R.S., and by R. D. Oldham, F.R.S. Some of these camouflets damaged a few of our galleries, but the big mines as a whole were preserved intact for the most part until the day they were to be sprung.

"The fact that all the tunnelling companies of the Second Army were able to drive their long tunnels, in many cases far under the German lines, and lay 22 enormous mines each filled with from a few tons up to 40 tons of ammonal, without the Germans being able to locate the mines, is obviously a grand tribute to the loyalty of some 8,000 miners, to each of whom the whereabouts of some of these mines was known, and was also a splendid proof of the high efficiency of Captain Pollock's organisation of the training of the observers for locating with his instruments the exact position of the enemy's countermines. At last, after over a year of waiting for many, there came for our miners 'Der Tag.'

"Before the phantom of false morning died on July 7, of 1917, the Second Army was tensely watching as 'Zero' approached for the flaring up of the great mines. Zero came, but for the moment there was no outward and visible sign that the great mines had been fired, but instantly the soles of our feet thrilled to the shock as of a great earthquake. A moment later the earth was rent open, 19 gigantic red roses sprang suddenly from the ground and as their crimson petals fell apart flames of all colours of the rainbow ending in brilliant white towered upwards. It recalled the Wars of the Roses, and after the white came black. Great columns of clay, sand, masonry, ferro-concrete and machine guns were hurled skywards, the air far and wide resounding with dull booms and roars like thunder. Nineteen German strongholds had been demolished in the twinkling of an eye.

"The ridges of Messines and Wytschaete, so fortified as to seem hope-

lessly impregnable for us, were stormed by our troops with a loss about one-fifteenth that sustained by our forces at Loos, and with a gain far transcending that of Loos.

"General Ludendorff admits in his book on the War that the explosion of these mines dealt a staggering blow to the morale of the German troops.

"To the success of this, the greatest piece of military mining that the world has ever seen, many men, notably the Inspector of Military Mines, Brigadier-General R. N. Harvey, specially contributed, and certainly Captain Pollock's work to this end was as essential as it was efficient. He was specially mentioned in despatches, and later promoted to the rank of Major in recognition of his services. The Messines-Wytschaete mine explosions practically killed German military mining on the Western Front, and later the School of Mines of the Second Army was closed. After assisting actively in the work of trenching near Strazeele, after the Germans had taken Kemmel and were capturing Bailleul, Pollock was transferred by special request of the War Office to Bookham, near Farnborough, in order to apply his knowledge of physics to methods of orienting aeroplanes flying at altitudes of over 10,000 feet, without the aid of direct observation of known objects on the earth's surface, and without the help of the compass. He was making some progress with this work when his further experiments were stopped by the Armistice on November 11, 1918.

"The War ended and with it his war service; he hastened back to his University duties. Words fail to do justice to so modest and yet so strong and chivalrous a character. If one uses the term gentleman in the sense of one whose courtesy and consideration for others in whatever walk of life is unvarying, who always places the good of others before his own, and who is a modest, earnest student and lover of nature, and his fellow-man, then the late Professor Pollock was indeed, whether in war or peace, a great gentleman, such an one as we delight to honour, aspire to follow and would ever hold in loving memory."

Sir Edgeworth David's splendid appreciation must not be taken merely as a tribute to a departed friend, but as a most true, just and sober description of Arthur Pollock's great character; he might indeed have added that he was one of the most affectionate sons, brothers and friends that ever walked the earth, and yet a man of iron firmness and determination in any course which his considered judgment led him to adopt.

Pollock's death was caused by blood-poisoning originating in a cut finger; it led to pneumonia and death within three days while he was still at the height of his activity and powers. He never married.

Scientific Work.

It was characteristic of Pollock that, first as a student and then as a Demonstrator, he subordinated his own experimental work to the task of helping on what was in hand in the laboratory. It thus happened that his earlier papers were written in collaboration with R. Threlfall, and mainly dealt with improvements in apparatus and the ascertainment of the electrical constants of substances in a known state of chemical purity. Following Hertz's discovery of the mode of production of electric waves many experiments were made with the idea of increasing the energy of the waves, and at the same time devising better means for their detection. These experiments were never published, but led, at a later date, to a paper on the relation between the wave-lengths of the emitted radiation and the geometrical constants of the systems in which they were set up.

Between 1888 and 1898, however, the main experimental work was an endeavour to make a portable instrument which should indicate the intensity of gravity by inspection. This work was carried out in conjunction with R. Threlfall and was in the highest degree arduous and difficult. ('Phil. Trans.,' A, vol. 193, 1899.) The principle employed was as follows:—

A quartz thread was stretched between two points. One was fixed, and the other (the axle of the arm of a sextant) could be rotated so as to twist the thread through a known angle. At the centre of the thread a short length of fine wire was soldered so as to lie at right angles to the thread. The thread being stretched horizontally it was twisted so as to cause the bit of wire to lie horizontally also. Just before the wire topples over it is in a position of small stability. In the elaborate instrument constructed on the above principle the bit of wire is brought to a fixed position near the horizontal plane, and the measurement consists in determining how much the thread has to be twisted to secure this result at various places where the value of gravity is sought. It was found best to calibrate the instrument by taking readings at two places where "g" had different known values. In the progress of the work it was discovered that fused quartz was only just good enough—or hardly good enough—for the purpose, and most laborious experiments had to be made to find what was the best relation of the length of thread to its diameter and the relation of both these to the load (*i.e.*, the weight of wire) to make the progressive yield of the quartz a minimum. Those trials necessitated great manipulatory skill, and Pollock soon outstripped his partner in this, and thereby assumed the greater burden of the undertaking.

The Gravity Balance was carried to Tasmania and many other places, but a great projected journey to the North Coast of Australia had to be given up as the result of an unlucky accident to the instrument the day before the journey should have begun. Repairs could not be effected in time for a journey during that vacation, and no opportunity ever recurred as

Threlfall left Australia soon after. The instrument remained in Pollock's hands but he made no further use of it, his interests having taken other directions. With the experience obtained it should now be possible to construct a fresh instrument making use of "invar" which would get rid of most of the difficulties encountered in the first instrument. The main remaining difficulty would be to find anyone with Pollock's enthusiasm and manipulative skill. During the years 1895—1898 Pollock made many trials of experimental methods for a book Threlfall was writing on the subject, it having been decided to recommend no method that had not been actually tried out.

On becoming Professor of Physics, Pollock at first followed up some work on the determination of Specific Inductive Capacities in conjunction with O. U. Vonwiller. For this purpose the experience he had already had with electric waves proved of service. ('Phil. Mag.,' June, 1902–6 Series, vol. III, No. 18, pp. 586–606.)

The measurement of electric waves in relation to the dimensions of the oscillators occupied him off and on for several years and led to several papers *i.e.*, 'Journ. Roy. Soc., N.S.W.,' 1903–04, vol. 37, pp. 198–224; 'Engineering,' November 13, 1914, vol. 98, p. 581; 'Journ. Roy. Soc., N.S.W.,' 1915, vol. 49, p. 2 and pp. 253–257. This work put the relation of the wave length to the dimensions of straight wires, and wires bent into circles and into rectangles, on a sounder basis than it had been before and was very welcome at the time. It was followed by papers on the crushing of a hollow lightning conductor by the discharge (with S. H. Barraclough), and on a simple form of Sprengel Vacuum pump in which the supply of mercury is kept up by distillation.

The next subject investigated was the discharge of electricity from glowing carbon 'Journ. Roy. Soc., N.S.W.,' vol. 42, p. 201, with A. B. B. Ranclaud, and 'Phil. Mag.,' 1909, vol. 17, p. 366. This was followed by a paper on the "Relighting of the Carbon Arc," 'Phil. Mag.,' vol. 17, p. 449 (1909). In the first of these papers the conditions under which the non-luminous discharge changes to a luminous one are investigated. In 'Phil. Mag.,' vol. 18, p. 229, the discontinuity of potential at the surface of glowing carbon was investigated and a formula for its evaluation arrived at. The papers were all written in conjunction with students.

In 1909 began the work on the ions of the atmosphere which constitutes Pollock's most original and important contribution to science, and his results were communicated to the Royal Society of New South Wales in 1909, to the Australian Association for the advancement of Science 1909, 1910, and summarised in 'Phil. Mag.,' 1915, vol. 29, p. 514, and vol. 29, p. 636. Langevin discovered in 1905 that large ions of a mobility of about one-three-thousandths exist in the air alongside of the gas ions of mobility of about 1·5. By careful observations carried out over a long period Pollock discovered that there were present in some cases other ions with a mobility of about one-fiftieth, and he

showed ('Journ. Roy. Soc., N.S.W.,' vol. 43, p. 198, 1909) that the mobility of the largest class of ions depends on the humidity of the air as had been suggested as likely by Rutherford. It had also been shown by observations in his laboratory that large ions are not formed in dust free air during periods measured in days. These facts led Pollock to picture the Langevin ion as a dust particle to which a small ion is attached, the dust particle being surrounded by a collection of water molecules. The question then arose—do these water molecules represent liquid or gaseous water? To settle this point observations were made of the mobilities at various temperatures, pressures, and degrees of saturation, and a thermodynamic theory was developed by the investigation of a mixture of air, ions and water vapour used as the working fluid in a reversible engine. The argument cannot be abstracted but it led to a certain relation between the mobilities of the ions and the degree of saturation of the air on the supposition that the water molecules were present as liquid, *i.e.*, that they had a latent heat of evaporation equal to that of water. A discussion of the experimental results showed that these were in conformity with this theory, and hence Pollock concluded that the adsorbed water exists as liquid water.

A similar argument applied to the data he obtained for intermediate ions led to the result that here the water is probably adsorbed in the gaseous state and in this case experiment showed that the mobility is determined by the actual vapour pressure of the water present rather than on the relative humidity. This conclusion was strongly supported by the fact also discovered by Pollock that the large—*i.e.*, Langevin's—and intermediate—*i.e.*, Pollock's—ions co-exist at pressures below seventeen millimetres of mercury, but above this pressure large ions only are to be found. The result of this work was a definite advance in our knowledge of the ions of the atmosphere and the work itself forms a good illustration of Pollock's powers as a Physicist.

About 1910 Pollock was consulted in connection with some litigation over flotation processes of ore separation, and this led him to consider the problem of the formation of froth. Papers on the "Origin of the small bubbles of froth" appear in 'Journ. Roy. Soc., N.S.W.,' 1911 and 1912, vol. 45, pp. 2 and 204, and an abbreviated communication in 'Phil. Mag.,' 1912, vol. 24, p. 189. A photographic method was developed which shows clearly how small bubbles come to be formed, but the paper does not call for further comment here.

At the time of his death Pollock was engaged in some acoustical work suggested by his experiences in France, and in co-operating with the architect in the design of a new Physical Laboratory, planned on a very generous scale, for the University of Sydney. He was never more active and full of ideas than at the time of his death, in fact, the writer had just received from him a full description of the proposed Laboratory, with plans and wise comments, when the news of his death reached England.

R. T.

CAMILLE JORDAN, 1838-1922.

Camille Jordan, who died on January 20, 1922, at the age of 84, was one of the great French mathematicians of the nineteenth century. His life was not notably more eventful than that of most mathematicians. He was professor at the École Polytechnique from 1876 to 1912, and also at the Collège de France; a member of the Institute from 1881, and editor of the 'Journal de Mathématiques' ('Liouville's Journal') from 1885. He was elected a Foreign Member of the Society in 1919.

Jordan was a mathematician of great profundity and originality, and left behind him contributions of the first importance to every field in which he worked. He is, no doubt, best known now for his 'Cours d'Analyse,' the celebrated treatise in which, according to the admirable custom of the best French mathematicians, he embodied the substance of his professorial lectures. This work, 'Cours' though it is, is no mere text-book, but contains the substance of the main researches of Jordan's later life, and it is a rare tribute to the fundamental character of these researches that, in so general a treatise, they should seem so perfectly in place.

Jordan's 'Cours' was the first systematic treatise on analysis in which the fundamental problems of the theory of functions were envisaged from a really modern point of view, and it has accordingly played a great part in the education of most of the leading analysts of the day. It was in its second edition, of 1893–1896, that it assumed substantially its final form. The first edition had been comparatively undistinguished. "Dans la précedente édition, où nous tenions à conserver toute la simplicité possible, nous avions glissé un peu rapidement sur les premiers principes . . .", Jordan remarks himself: but now "nous les exposons avec toute la précision et la généralité que nous avons pu, dût-il en résulter quelque complication . . ." The result was a new book and the rise of a new school; for it is fair to attribute to the inspiration of Jordan the beginnings of the movement which, carried on by Hadamard, Borel and Lebesgue, has revolutionised the foundations of modern analysis.

The book, for all its masterfulness, is by no means a very easy one to read. Jordan, I imagine, was no believer in easy roads to the understanding of mathematical truth; he could not shirk a difficulty himself, and he had no intention of allowing his readers to do so. A writer of a text-book, if he be ingenious and competent enough, can often turn a dangerous mathematical obstacle, and lead his army of readers in perfect order to an easy victory, while formidable fortresses lie still unreduced behind him. Jordan invariably scorns such temporary triumphs, knowing too well the disastrous consequences of any later check. Every difficulty, as it arises, must be fairly faced and definitely conquered, and all the ground consolidated in the rear.

Jordan's ideal is, unquestionably, the right one, and it is because he followed it so consistently that his book has been, to the best of mathematical students, so signal an inspiration. To have read it and mastered it is a mathematical education in itself; and it is hardly possible to overstate the influence which it has had on those who, coming to it as I did from the elaborate futilities of 'Tripos' mathematics, have found themselves at last in presence of the real thing. But the ideal is a difficult one, and it is just possible to be too uncompromising in its pursuit. There are times when a little pedagogic ingenuity is innocuous and even useful, and Jordan is apt to push his scorn of it a little too far. He tends to neglect simplicity and symmetry of presentation, even when it might be attained quite easily and without any real surrender of the end in view. It was said of him, by his pupils at the École Normale, that "lorsque M. Jordan rencontre dans un raisonnement quatres quantités jouant enactement le même rôle, il les designe par u, A'', λ, e_3."* It is of course a humorous exaggeration, but it has a foundation of justice: "nous avions du moins senti nettement combien M. Jordan se soucie peu de certaines précautions pédagogiques vulgaires . . ."

Among the many individual investigations embodied in the book, there are two which stand out now for originality and for a fruitfulness still quite unexhausted. There is a good deal in the early chapters, the theory of "content," and so on, that has now been superseded; but we shall certainly never forget the function of bounded variation or the continuous Jordan curve. A function $f(x)$, defined in an interval (a, b), is of bounded variation if, when we divide the interval into parts in any manner by points $x_0 = a, x_1, x_2, \ldots, x_n = b$, the sum of the absolute values of the increments $f(x_{i+1}) - f(x_i)$ of the function is less than a number independent of the number or nature of the divisions. It is characteristic of such a function that it can be expressed as the difference of two steadily increasing functions, so that the concept is a generalisation of one of the simplest in mathematics. The generalisation may seem an obvious one, but it is one of the great generalisations which carry simplicity and symmetry in their train. The "monotonic" (increasing or decreasing) function has, for analytical purposes, a fatal defect, namely, that its characteristic property is not invariant for the elementary operations; the sum, for example, of two monotonic functions is not in general monotonic. Functions of bounded variation, while retaining the most essential characteristics of monotonic functions, form a group for these operations, and their introduction gives to the solutions of a large number of important problems a symmetry and unity which would otherwise be quite unattainable. The classical example is that of Dirichlet's conditions for the convergence of a Fourier's series. There is something anomalous in Dirichlet's demonstration, admirable as it is. It is not true that, if Dirichlet's conditions are satisfied by f and g individually,

* I quote from a review of the third edition of the 'Cours' (1915), by M. Lebesque.

they are also satisfied by $f+g$; while the *result*, if true for two functions, is obviously true also for their sum; the conditions break down and yet the result remains. It was this anomaly that Jordan set himself to remove, and from which his discovery originated.

There is another familiar example of the use of the concept of bounded variation, which shows in a striking manner the connection between different parts of Jordan's work. What is the condition that a continuous curve should have a length? A continuous curve is a set of points (x, y) defined by equations

$$x = x(t), \quad y = y(t),$$

where $x(t)$ and $y(t)$ are continuous functions of a parameter t. The precise definition is Jordan's, and a continuous curve, as so defined, still carries the name of a *Jordan curve.* The *length* of a curve is the limit of the perimeter of an inscribed polygon, and the problem is that of finding the conditions that this limit should exist. There is a complete solution: the curve is rectifiable (possesses a length) if and only if $x(t)$ and $y(t)$ are functions of bounded variation. So perfect is the solution, and so inevitably does the concept of bounded variation intervene, that it is difficult to imagine how the concept came to be invented for an entirely different purpose.

Any mention of the *Jordan curve* suggests inevitably the most famous of all the theorems with which Jordan's name is connected. What is meant by the *inside* or the *outside* of a closed curve? How can these notions be defined precisely, and the rough intuitions of geometrical "common sense" translated into accurate analytical terms? Jordan's solution of the problem is not absolutely complete, but it was he who put the question, stated the solution, and provided the essentials for the first accurate proof. The problem was no doubt suggested to him by his early "topological" researches. A simple closed continuous curve C is a set of points (x, y) in two dimensional space, defined by $x = x(t)$, $y = y(t)$, where t is a parameter which varies, say, from 0 to 2π, and $x(t)$, $y(t)$ are continuous functions such that

$$x(t_1) = x(t_2), \quad y(t_1) = y(t_2)$$

if and only if t_2 is congruent to t_1 to modulus 2π. Such a curve divides the plane into two regions, D_1 and D_2, of which C is the common boundary. If P and Q are points of the same region, then there is a continuous curve PQ which has no point in common with C; but if they lie one in D_1 and one in D_2, then any such curve must meet C once at least. This is Jordan's theorem, the most famous theorem in 'Analysis Situs,' and the source of a whole branch of modern mathematics. Jordan's proof is incomplete, since he assumes the truth of the theorem for a simple polygon, and the success of his attempt to free himself from the pre-suppositions of geometrical intuition is therefore incomplete. The gap has been filled by his successors by the construction,

both of alternative demonstrations in which no such preliminary assumption is required, and of elementary inductive arguments specially applicable to the polygonal case; but the theorem remains justly and permanently associated with his name.

I have written of Jordan as an analyst, and it is no doubt as an analyst that he won the most permanent fame. But even his analysis bears continual witness, in his selection of problems and in the spirit in which he pursues them, to the interests which occupied him in his earlier life. The notion of a group, whether abstract or a group of algebraical or geometrical transformations, is never long absent from his mind, as anyone who has studied his admirable account of the elliptic functions will remember; and his early researches are almost entirely dominated by the theory of groups.

In his 'Traite des Substitutions et des Équations Algébriques,' published by Gauthier-Villars in 1870, Jordan gave the first comprehensive account of the theory of Galois ("dont tout ceci n'est qu'un commentaire") and its applications to the theory of algebraic equations, with chapters, on a less extensive scale, on geometry and elliptic functions. The treatise is occupied for the most part with groups of linear substitutions. In the last book he solves a problem put by Abel, that of finding all equations of a given degree which are soluble by radicals, and of deciding whether a given equation belongs to this class or not. But there are also very important original contributions to the general theory, in particular concerning primitive groups and factors of composition. A series of memoirs published later complete and extend his results. Only an expert in the theory could venture to pass judgment on Jordan's contributions to it, and I must be content to repeat the verdict of one of the most distinguished of his countrymen, that in his treatise he showed himself "un grand algébriste," with "une rare profondeur d'esprit et une extraordinaire puissance d'abstraction," who "se jouait au milieu des discussions les plus subtiles, se plaisant à aborder les questions dans toute leur généralité, comme s'il craignait que quelque particularité l'empêchat de voir les vraies raisons des choses." It is at any rate a verdict which no one who knows Jordan as an analyst will be inclined to dispute.

G. H. H.

CHARLES NIVEN, 1845-1923.

PROF. CHARLES NIVEN was born at Peterhead in September, 1845; he belonged to a family of remarkable ability, four of whom were Wranglers. At the age of fourteen he went to King's College, Aberdeen, where he graduated in 1863. Thereafter he went up to Trinity College, Cambridge, and was Senior Wrangler in 1867. In the same year he was elected a Fellow of his College and appointed Professor of Mathematics at Cork.

The time when he was an undergraduate at Cambridge was one of great activity in mathematical physics. Maxwell's classical memoir, "A Dynamical Theory of the Electromagnetic Field," appeared in 1865; the representation of physical phenomena dynamically was being rapidly extended, and the suitability of Lagrange's methods for such representations more widely recognised. This influence is clearly marked in Professor Niven's scientific work; his first paper "On the Application of Lagrange's Equations to the Solution of Questions of Impact," published in the 'Messenger of Mathematics' in 1868, demonstrated the advantages of Lagrange's method in such problems. A succession of papers followed on subjects covering a wide range—the wave surface, the theory of elasticity, the parallax of double stars, conduction of heat and electricity. In these papers, more especially in the two papers published in the 'Philosophical Transactions,' "On the Conduction of Heat in Ellipsoids of Revolution," 1881, and "On the Induction of Electric Currents in Infinite Plates and Spherical Shells," 1882, great analytical power is shown, though the analysis is not allowed to obscure the real objective of the investigations.

In 1880 Prof. Niven was appointed to the Chair of Natural Philosophy in the University of Aberdeen, and with his transference to Aberdeen his activity in research work was necessarily diminished. The changes which were made in the arrangement of the work of a Scottish University after his appointment left little leisure to the occupants of some of the chairs, Natural Philosophy being one of those affected by the changes; whether these changes have proved beneficial to the students is somewhat doubtful, but that the changes have rendered it almost impossible for the Professors in question to find time both for original investigations and for the efficient discharge of their teaching duties is certain.

During Professor Niven's long tenure of the Chair of Natural Philosophy the department has grown considerably; at the beginning of his term of office it was inadequately housed at King's College, but the department is now at Marischal College, where new laboratories were built for it towards the end of last century, and it was largely owing to him that this improvement was carried out. Formerly instruction in experimental physics was of necessity

confined to a small number; with the greater facilities at Marischal College a larger number can have practical training and consequently a more thorough instruction in Natural Philosophy.

Professor Niven's many students appreciated his unsparing efforts on their behalf; the greater part of every day during term found him in his department engaged either in teaching or in preparing the demonstration experiments for the next lectures, and apart from occasional fishing expeditions he was there during the vacations also.

In the spring of 1922 he became seriously ill, and, although he was able to take some of his honours classes at his house during the summer term, he retired from the Professorship at the end of the academical year. To the regret of his many friends he did not enjoy a long evening of leisure; gradually becoming weaker, he died on May 11, 1923.

H. M. M.

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ERRATA.

Pl. 20 (fig. 9), *for* (× 2¼) *read* (× 3).
P. 276, line 18, *for* (*loc. cit.* p. 1) *read* (*loc. cit.* p. 272).

END OF THE HUNDRED AND FOURTH VOLUME (SERIES A).

Harrison and Sons, Ltd., Printers in Ordinary to His Majesty, St. Martin's Lane.